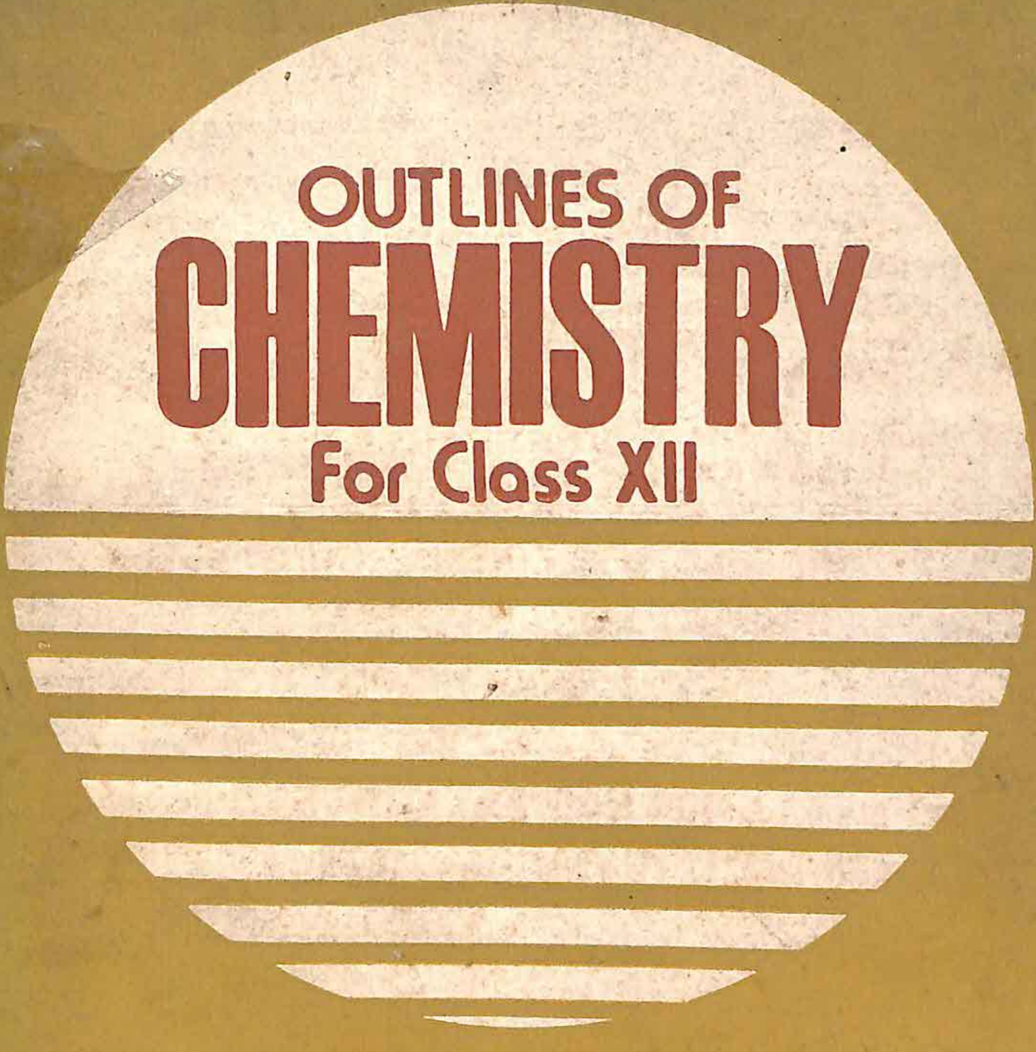


OUTLINES OF CHEMISTRY

For Class XII

M KATYAL R P KATYAL

OUTLINES OF CHEMISTRY

McGraw-Hill Offices

New Delhi
New York
St Louis
San Francisco
Auckland
Bogotá
Guatemala
Hamburg
Lisbon
London
Madrid
Mexico
Montreal
Panama
Paris
San Juan
São Paulo
Singapore
Sydney
Tokyo
Toronto

(Recommended by the Central Board of Secondary Education vide letter No. Acad II/GR II/PF/86/9679)

OUTLINES OF CHEMISTRY

for Class XII

M KATYAL
St. Stephen's College
Delhi University, Delhi

R P KATYAL
Govt. College
Rohtak

S. C. E. R. T. West Bengal
Library
Calcutta
25/3, B. C. Road

Tata McGraw-Hill Publishing Company Limited
NEW DELHI

C.E R.T, W.B. LIBRARY
te 10.8.98
cn. No. 9680

© 1980, TATA McGRAW-HILL PUBLISHING COMPANY LIMITED

First impression 3300
First reprint 2200 copies June 1983
Second reprint 1600 copies Jan. 1987

No part of this publication can be reproduced in any form or by any means without the prior written permission of the publishers

This edition can be exported from India only by the publishers, Tata McGraw-Hill Publishing Company Limited

Published by Tata McGraw-Hill Publishing Company Limited,
12/4 Asaf Ali Road, New Delhi-110 002 and printed at
Ram Printograph (India), New Delhi 110 020

Preface

We were invited by the publishers to write a book on chemistry which would meet the needs of class XII students. We gladly accepted this assignment and proceeded with the writing of the text. An attempt was made to present the subject in a manner which is systematic, clear and easy to understand. We have tried to be concise in our discussion but not at the cost of omitting topics from the prescribed syllabus. With the help of numerous illustrations, we have endeavoured to make the study of chemistry an active, visual experience. How far we have been successful in this attempt will be decided by our colleagues who are teaching this course and the students for whom the book is primarily meant. We look forward to their comments and suggestions for modifications and improvements.

We sincerely thank all our colleagues for their suggestions during the preparation of the manuscript. We also express our sincere gratitude to our families for their encouragement and forbearance.

M KATYAL
R P KATYAL

Monsoon, 1980

तमसोमा ज्योतिर्गमय

Lead me from Darkness to Light

Contents

Preface v

1. **More about Atoms** 1

1.1. Dual nature of radiation and matter 1; 1.2. De Broglie equation 3; 1.3. The uncertainty principle 4; 1.4. Atomic orbitals 6; 1.5. Quantum numbers 7; 1.6. Shapes of orbitals 10; 1.7. Electronic configuration of atoms 13

2. **More about Molecules** 22

1.2. Molecular orbital method 21; 2.2. Structures of simple diatomic molecules 27; 2.3. Hybridization 31; 2.4. Bond distance 34; 2.5. Bond energy 35

3. **More about State of Matter** 38

3.1. Classification of solids 38; 3.2. Study of crystals by x-rays 40; 3.3. Space lattice and unit cell 42; 3.4. Crystal systems 43; 3.5. Packing of constituent particles in crystals 45; 3.6. Ionic crystals 48; 3.7. Defects in crystals 49; 3.8. Electrical conductance in solids 52; 3.9. Alloys 53; 3.10. Liquid crystals 53.

4. **More about Chemical Energetics** 56

4.1. Conservation of energy 56; 4.2. Internal energy, E 57; 4.3. Enthalpy, H 57; 4.4. Spontaneous chemical change 58; 4.5. Causes of spontaneity 59; 4.6. Entropy, S 60; 4.7. Entropy of fusion 61; 4.8. Entropy of vapourization 61; 4.9. Free energy 62; 4.10. Physical significance of free energy 63; 4.11. Conditions for equilibrium and spontaneous changes 64; 4.12. Relation between probability of a process and temperature 64; 4.13. Prediction for the sign of ΔH 64; 4.14. Prediction for the sign ot ΔS 65

5. **Kinetics** 67

5.1. Fast and slow reaction 67; 5.2. The reaction rate 68; 5.3. The rate law 69; 5.4. First order reaction 71; 5.5. Half life period 72; 5.6. Order and molecularity of a reaction 73; 5.7. Factors influencing rate of reaction 74; 5.8. Reversible reactions 82; 5.9. Enzyme catalysts 82

6. **Solutions** 86

6.1: Types of solutions 86; 6.2. Models of expressing concentrations of solutions 88; 6.3. Vapour pressure of solutions 89; 6.4. Ideal solutions 81; 6.5. Non-ideal solutions 91; 6.6. Colligative properties 95: 6.7. Molecular masses from colligative properties 103; 6.8. Abnormal molecular masses 104

7. **Electrochemistry** 107

7.1. Redox reaction 107; 7.2. Electrochemical cell 108; 7.3. Functions of salt bridge 110; 7.4. Other galvanic cells 110; 7.5. Cell notations 111; 7.6. Electrode potentials 111; 7.7. Electrochemical series 113; 7.8. Nernst equation 114; 7.9. Calculation of cell potentials from electrode potentials 115; 7.10. Some energy producing cells 116

8. **Surface Chemistry** 119

8.1. Adsorption 119; 8.2. Adsorption of gases on solids 122; 8.3. Competing adsorption 125; 8.4. Adsorption of solutes from solutions 126; 8.5. Applications of adsorption 126; 8.6. Role of adsorption in catalytic reactions 127; 8.7. Colloidal state 127; 8.8. True solution, colloid and suspension 128; 8.9. Classification of colloidal solutions (sols) 128; 8.10. Multimolecular, macromolecular and associated colloids 130; 8.11. Preparation of colloidal solutions 131; 8.12. Purification of colloidal solutions 133; 8.13. Properties of colloidal solutions 135; 8.14. Origin of charge on colloids 138; 8.15. Coagulation of colloidal solutions 138; 8.16. Hardy-Schulze rule 139; 8.17. Interaction between colloids 140; 8.18. Emulsions 141

9. **The Oxygen Family** 143

9.1. General trends 143; 9.2. Compounds 147; 9.3. Structure of oxygen molecule 148; 9.4. Ozone 149; 9.5. Sulphuric acid 152; 9.6. Sodium sulphite 158

10. **The Halogen Family** 161

10.1. General trends 161; 10.2. Occurrence of halogens 166; 10.3. Uses of halogens 167; 10.4. Hydrogen halides 167; 10.5. Oxides and oxyacids of halogens 168; 10.6. Positive oxidation state of halogens 169; 10.7. Fluorine 170; 10.8. Hydrogen fluoride 172; 10.9. Interhalogens 172; 10.10. Polyhalides 173; 10.11. Bleaching powder 173; 10.12. Sodium hypochlorite 174

11. **Nuclear Chemistry** 176

11.1. Radioactivity 176; 11.2. Types of radioatoms 177; 11.3. Group displacement law 178; 11.4. Chemical for nuclear charges 181; 11.5 Radioactive disintegration series 182; 11.6. Artificial transmutation 182; 11.7. Disintegration rate and disintegration constant 183; 11.8. Half-life period 184; 11.9. Carbon dating 187

12. **The Noble Gases** 191

12.1. Discovery of noble gases 191; 12.2. General trends 192; 12.3. Isolation 195; 12.4. Uses 196; 12.5. Noble-gas compounds 198; 12.6. Structures of xenon fluorides 199

13. Metallurgical Operations 202

13.1. Occurrence of metals 202; 13.2 Metallurgy 203

14. The Transition Elements (d-Block Elements) 219

14.1. Definition and electronic configurations 219; 14.2. General characteristics 221; 14.3. Nomenclature of complexes 225; 14.4. Metals of scandium group 227; 14.5. Metals of titanium group 227; 14.6. Metals of vanadium group 228; 14.7. Metals of chromium group 228; 14.8. Chromium compounds 229; 14.9. Metals of manganese group 230; 14.10 Manganese compounds 231; 14.11. Metals of group VIII 232; 14.12. Iron and steel 233; 14.13. Alloy steels 234; 14.14. Iron compounds 234; 14.15. Corrosion 238; 14.16. Metals of copper group 241;, 14.17. Properties of copper group metals 242; 14.18 Uses of copper group metals 244; 14.19 Compounds of copper 245; 14.20 Compounds of silver 246: 14.21 Metals of zinc group 247; 14.22 compounds of zinc group metals 248

15. Alkyl and Aryl Halides 251

15.1. Nomenclature 252; 15.2. Isomerism 253: 15.3. Preparation of alkyl halides 259; 15.4. Preparation of aryl halides 261; 15.5. Industrial preparation 262; 15.6. Physical properties 263; 15.7. Chemical properties 266; 15.8. Polyhalogen derivatives 273; 15.9. Dihalogen derivatives 273; 15.10. Trihalogen derivatives 275

16. Compounds with Functional Groups Containing Oxygen 279

16.1. Alcohols and phenols 280; 16.2. Nomenclature 281; 16.3. General methods of preparation 282; 16.4. Physical properties 286; 16.5. Chemical properties 287; 16.6. Methods for distinguishing alcohols 294; 16.7. Tests for phenols 295; 16.8. Absolute alcohol 295; 16.9. Industrial alcohol 296; 16.10. Toxicity of alcohols 296; 16.11. Uses of alcohols and phenols 296; 16.12. Ethers 297; 16.13. Nomenclature 297; 16.14. General methods of preparation of ethers 298; 16.15. Physical properties of ethers 299; 16.16. Chemical properties of ethers 300; 16.17. Uses of ethers 302; 16.18. Aldehydes and ketones 302; 16.19. Nomenclature 303; 16.20. Structure of carbonyl group 304; 16.21. General methods of preparation of aldehydes and ketones 305; 16.22. Industrial preparation of some aldehydes and ketones 308; 16.23. Physical properties of aldehydes and ketones 309; 16.24 Chemical properties of aldehydes and ketones 310; 16.25. Tests for aldehydes and ketones 317; 16.26. Carboxylic acids 317; 16.27. Nomenclature 318; 16.28. General methods of preparation of carboxylic acids 319; 16.29. Industrial preparation of some carboxylic acids 320; 16.30. Physical properties of carboxylic acids 322; 16.31. Chemical properties of carboxylic acids 322: 16.32. Functional derivatives af acids 329; 16.33. Methods of preparation of functional derivatives of acids 331; 16.34. Physical properties of acid derivatives 333; 16.35. Chemical properties of acid derivatives 333

17. Compounds with Functional Group Containing Nitrogen 337

17.1. Amines 337; 17.2. Nomenclature 338; 17.3. Laboratory preparation 339; 17.4. Industrial preparation 341; 17.5. Physical properties 341; 17.6. Chemical properties 343; 17.7. Detection of amines 351; 17.8. Uses of amines 351; 17.9. Nitro compounds 352; 17.10. Preparation 352; 17.11. Physical properties 353; 17.12. Chemical properties 354; 17.13. Uses of nitro compounds 356

18. Polyfunctional Organic Compounds **358**
18.1. Polyhydric alcohols 358; 18.2. Ethylene glycol 359; 18.3. Glycerol 362; 18.4. Oxalic acid 366; 18.5. Glycine 369

19. Biochemistry **374**
19.1. Carbohydrates 374; 19.2. Lipids 378; 19.3. Vitamins 380; 19.4. Hormones 381; 19.5. Proteins 382; 19.6. Nucleic acids 385

20. Chemistry in the Service of Man **390**
20.1. Agricultural compounds 390; 20.2. Polymers 395; 20 3. Soaps and detergents 402; 20.4 Medicinal compounds 405; 20.5. Chemotherapy 406

Unit 1

More about Atoms

Dual nature of particle and radiation (photoelectric effect, etc.) de Broglie, equation, uncertainty principle, quantum numbers, Hund's rule, Pauli's exclusion principle.

The study of electronic structures or electronic configurations of atoms provides explanation for the chemical behaviour of atoms. We are already familiar with some concepts of electronic structure. In this Unit we shall study some more aspects of the subject and learn about the behaviour of electrons.

Based on Planck's quantum theory, the Bohr's model of an atom could successfully explain the hydrogen-like spectra. However, it suffered from several limitations and could not explain the spectral details of multielectron atoms. It could not account for the shapes of molecules arising out of the directional bonding between atoms. The modern wave mechanical model (*wave mechanics*) now replaces the Bohr's theory and provides suitable explanation for the spectral characteristics of all types of atoms.

1.1. DUAL NATURE OF RADIATION AND MATTER

It is seen that both radiation and matter behave sometimes like particles and sometimes like waves. In other words, we can say that they exhibit a dual behaviour. Certain phenomena like photoelectric effect, can be explained if radiation has a particle nature whereas certain other phenomena such as interference, diffraction, etc., are explained if the radiation has a wave nature. Since radiation exhibits both photoelectric, interference and diffraction it is said to have a dual character.

Photoelectric effect

When light of a *certain frequency* strikes the surface of a metal, electrons are ejected from the metal. This phenomenon is called *photoelectric effect* (Fig. 1.1). Only a few metals show this effect under the action of visible light but many more show it under the action of more energetic ultraviolet light. Caesium with the lowest ionization energy amongst the alkali metals, rejects electrons easily when light strikes its surface. This metal is much used in photoelectric cells.

Photoelectric effect cannot be explained on the basis of the wave theory. According to this, energy of radiation depends on its intensity. If radiation of *any frequency* is made sufficiently intense, it should cause ejection of electrons. But this does not happen. The radiation striking the surface of a metal must have at least a certain minimum frequency, called *threshold frequency*, to cause the ejection of electrons. The frequency varies with the nature of the metal. In alkali metals, it is quite low (in the visible region) while in many others, it is quite high (in the ultraviolet region).

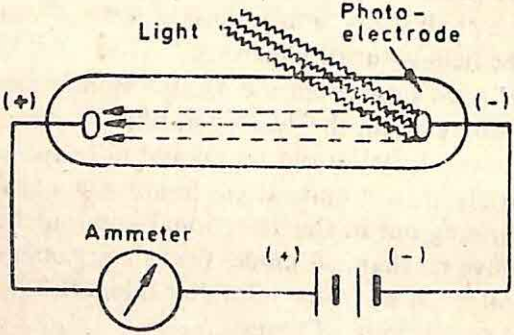


Fig. 1.1. Photoelectric effect. When the photoelectrode is irradiated by radiation, a current flows through the circuit as shown by ammeter.

Photoelectric effect can be explained by quantum theory. Suppose the threshold frequency of radiation required to eject an electron from a metal is ν. According to the quantum theory, this radiation will comprise of bundles of energy, the energy of each bundle being given by $h\nu$. These bundles are called photons. Photon has no mass. It is just like a packet or bundle of energy. When a photon of light of frequency ν strikes an electron in a metal, it imparts its entire energy ($=h\nu$) to the electron. This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus. If the frequency of the radiation is less than the threshold frequency, there will be no ejection of electrons. Suppose the frequency of the radiation falling on a metal surface is higher than the threshold frequency. The photon of this radiation will now impart more energy to the electron than that needed to break it away from the atom. The additional energy will be used to give a certain velocity (i.e., kinetic energy) to the ejected electron. The photoelectric effect thus makes us to ascribe *particle character* to radiation.

1.2. DE BROGLIE EQUATION

Louis de Broglie, in 1923, suggested that a similar duality, i.e., both particle and wave characteristics might exist for *material* particles like an electron, a proton, an atom or a molecule. He postulated that with every moving particle, there is an associated wave called a *matter wave*. Thus, a material object will possess both the particle and wave characteristics. The wavelength associated with such a wave may be calculated as follows:

Let us consider an electron. If it is supposed to have wave character, its energy will be:

$$E=h\nu \qquad (1.1)$$

where h is the Planck's constant and ν is the frequency of the wave.

If the electron is supposed to have the particle nature, its energy will be given, according to Einstein's equation, as:

$$E=mc^2 \qquad (1.2)$$

Combining equations (1.1) and (1.2), we obtain:

$$h\nu=mc^2 \qquad (1.3)$$

But $$c=\lambda\nu$$

or $$\nu=\frac{c}{\lambda}$$

Substituting the value of ν in equation (1.3), we get

$$h\frac{c}{\lambda}=mc^2$$

or $$\lambda=\frac{h}{mc} \qquad (1.4)$$

If instead of c which is the velocity of light, the velocity of the moving particle is taken as v, equation (1.4) will become

$$\lambda=\frac{h}{mv}=\frac{h}{p} \qquad (1.5)$$

Solution. From Heisenberg's uncertainty principle, we have:

$$\triangle x.\ \triangle p = \triangle x.\ m\triangle v = \frac{h}{4\pi}$$

$$(\text{since } \triangle p = m.\triangle v)$$

Therefore

$$\triangle v = \frac{h}{4\pi.\triangle x.\ m} = \frac{6.625\times10^{-34}}{4\times3.14\times10^{-10}\times9.1\times10^{-31}}$$

(since mass of electron, $m=9.1\times10^{-31}$ kg; $h=6.625\times10^{-34}$ J sec)

$$=5.8\times10^{5} \text{ m sec}^{-1}.$$

Thus the velocity is uncertain by 5.8×10^{5} m sec^{-1}. It is clear that talking about the trajectory of an electron with uncertainty in velocity by such a huge value is meaningless.

Example 1.3. Calculate the uncertainty in velocity ($\triangle v$) of a ball of mass 0.10 kg when its uncertainty in position ($\triangle x$) is given by 10^{-10} m.

Solution. As we have seen in the above example,

$$\triangle v = \frac{h}{4\pi.\ \triangle x.\ m} = \frac{6.625\times10^{-34}}{4\times3.14\times10^{-10}\times0.10}$$

$$=5.27\times10^{-24} \text{ m sec}^{-1}$$

This uncertainty in velocity is of negligible value compared to the unusal velocity of a ball. Thus the concept of trajectory is meaningful in this case. In such objects we can talk about the position and velocity simultaneously.

1.4. ATOMIC ORBITALS

The motion of an electron around the nucleus cannot be described in terms of *orbits*. An orbit means a definite path for the the electron and the concept of such a path is incorrect according to uncertainty principle. Three physicists Werner Heisenberg, Erwin Schrôdinger and Paul Dirac, in 1925, developed a theory, known as ***quantum mechanics***, which describes the motion of electrons around the nucleus in terms of a set of mathematical expressions which allow for the dual character of electrons. These expressions are called ***orbital wave functions*** or simply *orbitals*. These are denoted by the symbol ψ (pronounced as sy).

In the physical sense, the orbital of an electron is a part of space around the nucleus in which the particular electron spends most of its time and has a high probability of being found. There are regions where the chances of finding the electron are relatively greater. Such regions are expressed in terms of *cloud of negative charge.* Electrons in atoms are assumed to be vibrating in space, moving haphazardly but at the same time are constrained to lie in regions of highest probability for most of the time. The charge cloud concept simply describes high probability region. It is difficult to represent an orbital by a simple picture. In Fig. 1.2, a comparison is made between an orbit and an orbital. The intensity of dotting in orbital is proportional to the relative probability of finding the electron there.

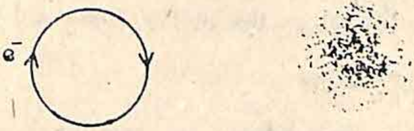


Fig. 1.2.

Orbit Orbital

1.5. QUANTUM NUMBERS

It has been found that for a particular orbital, the electron has a fixed energy. This is true whether an electron is in an atom or in a molecule. For an atom, the angular momentum of an electron is fixed. Thus, energy and angular momentum of an electron are quantized. These quantized values can be expressed in terms of so called *quantum numbers*. These numbers describe fully the allowed energies and general behaviour of an electron.

Each electron is characterized by four quantum numbers—the *principal* (n), *azimuthal* (l), *magnetic* (m_l) and *spin* (m_s). Each one of these quantum numbers is associated with a particular characteristic of the electron. The first three are derived from the wave equation whereas the fourth quantum number spin, arises from the direction of the spin of the electron.

Principal quantum number

This number, n, largely determines the energy of the electron (E_n) according to the formula:

$$E_n = -\frac{2\pi^2 me^4}{h^2 n^2}$$

where m is the mass of electron, e its charge, h the Planck's constant, and n the principal quantum number. Though the energy is generally spoken as energy of the electron, it is actually that of the electron-proton pair. The negative sign for energy shows that

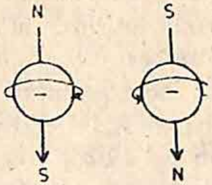


Fig. 1.4. Clockwise and anticlockwise spins of electrons about their own axis produce opposite magnetic fields.

Thus in each orientation, as per the magnetic quantum number, the number of electrons is two. Hence, the number of electrons in each energy level is $2n^2$ of its principal quantum number. An electron in an atom is completely described once its four quantum numbers have been specified.

Pauli's exclusion principle

This important Principle was advanced by Wolfgang Pauli, in 1925, and it states that *no two electrons in the same atom can be completely identical*. It means that no two electrons in an atom can be assigned the same combination of quantum numbers. For electrons with same values of n, l and m, the *spin* quantum number m_s, must be different, *i.e.*, $+\frac{1}{2}$ and $-\frac{1}{2}$. Thus in an orbital with specified orientation in space, there can be a maximum of two electrons and these must be of opposite spin.

We know that a given principal energy level (n) can have at the maximum n^2 orbitals and an orbital can have at the maximum two electrons. Thus, the maximum number of electrons in a principal energy level or shell is $2n^2$. Keeping in view the Pauli's exclusion principle and the limitation on the permitted values of quantum numbers, the number of electrons in an energy level can be calculated.

1.6. SHAPES OF ORBITALS

We have said earlier that an orbital of an electron is a part of space around the nucleus in which the particular electron has high probability of being found. This probability can be calculated in terms of orbital wave functions on the basis of the wave mechanical treatment. In the procedure, the *probability distribution curves* are obtained by plotting *radial probability distribution* (*i.e.*, the product of electron probability at a certain distance from the nucleus and the surface area sphere of the same radius) of the electron against distance, *r*, from the nucleus. The curve obtained in the case of 1*s* electron is shown in Fig. 1.5. It can be seen that the radial probability of finding an electron is zero at the nucleus (where $r = 0$). It increases as the distance increases, attains a maximum value and then decreases. In case of the hydrogen atom, the radial probability for 1 *s* electron is maximum at 0.53 Å from the nucleus (Fig. 1.5).

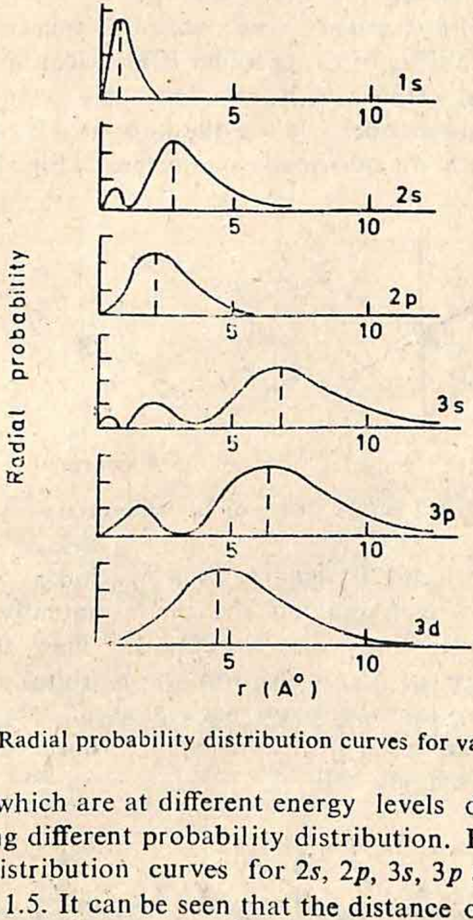


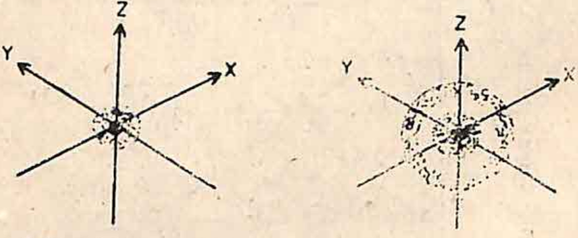
Fig. 1.5. Radial probability distribution curves for various orbitals.

Electrons which are at different energy levels differ from each other in having different probability distribution. For example, the probability distribution curves for 2*s*, 2*p*, 3*s*, 3*p* and 3*d* are also shown in Fig. 1.5. It can be seen that the distance of maximum probability for the 2*s* electron (2.7 Å) is close to that of the 2*p* electron (2.1 Å). It is, however, much larger than the distance of maximum probability for the 1*s* electron. This is consistent with the fact that 2*s* and 2*p* electrons are of approximately the same energy and this energy is greater than that of the 1*s* electron.

There is a peculiar little hump at 0.4 Å in the 2*s* distribution curve. This indicates that the 2*s* electron spends more of its time close to the nucleus than does the 2*p* electron. This accounts for the fact that the 2*s* electron is bound more tightly to the nucleus than the $2p$ electron, The overlapping of the distribution curves indicates that the outer electrons penetrate the region occupied by the inner electrons.

It may be noted that the number of peaks in the curves for the *s* orbital is equal to the *n* value, *i.e.*, 1 for $1s$, 2 for $2s$ and 3 for $3s$. In the curves for *p* and *d* orbitals, the number of peaks are $(n-1)$ and $(n-2)$, respectively.

The spatial distribution of an *s* electron is spherically symmetrical, *i.e.*, its probability of being found is identical in all directions from the nucleus. However, its size depends on the value of the principal quantum number. Thus, the $2s$ orbital is larger than the $1s$ orbital but both are spherically symmetrical (Fig. 1.6).

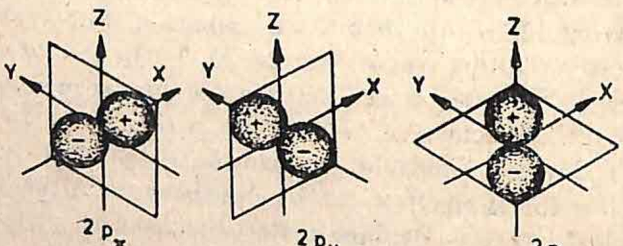


A 1s orbital

A 2s orbital

Fig. 1.6. The shapes of $1s$ and $2s$ orbitals.

The three *p* orbitals, designated as p_x, p_y and p_z, are of equal energy and are oriented along the three mutually right angled x—, y— and z-axes (Fig. 1.7). Keeping in view the probability distribution curve of the *p* electron, the *p* orbital may be thought as made up of two lobes, one on each side of the nucleus. The probability of finding the electron is equal in both the lobes. The shape looks like a dumb-bell.



$2p_x$

$2p_y$

$2p_z$

Fig. 1.7. Shapes and orientations of three *p* orbitals.

Thus, from the above representation, it may be inferred that each orbital can be pictured as an electron charge cloud or electron density. The directional character of p orbitals determines the geometry and properties of the molecules.

The five d orbitals, designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_z^2 possess equal energies and differ only in their orientations in three-dimensional space. Two of them, $d_{x^2-y^2}$ and d_z^2, have their greatest electron density in directions that lie along the axes. The $d_{x^2-y^2}$ orbital is oriented in the xy plane and has maximum probability along the x- and y-axes. while the d_z^2 is dumb-bell shaped and is oriented along the z-axis. The other three orbitals d_{xy}, d_{yz} and d_{xz} have their greatest electron density in the region between the axes. The shapes and spatial orientations of the d orbitals are represented in Fig. 1.8.

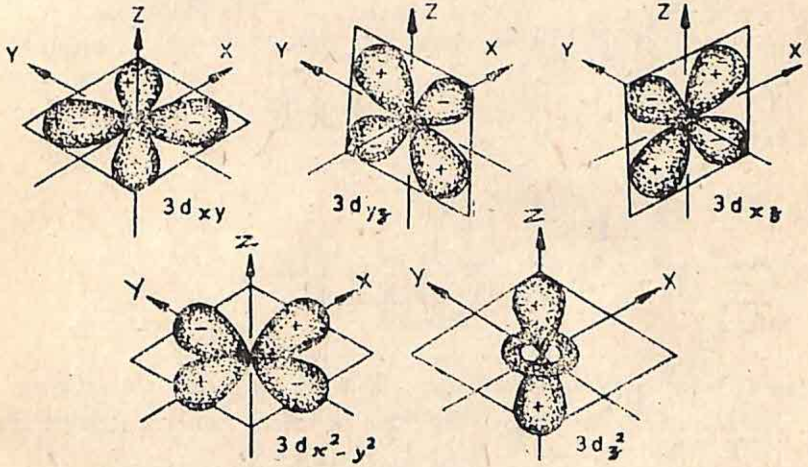


Fig. 1.8. Shapes and spatial orientations of five d orbitals.

1.7. ELECTRONIC CONFIGURATION OF ATOMS

We are already familiar with the rules of writing the electronic configuration of atoms. After learning about orbitals, it becomes appropriate to reconsider the topic and understand some additional features.

An atom in its lowest energy state (the stablest) is said to be in the *normal state* or the *ground state*. The filling of orbitals by electrons in the ground state of the atom is governed by the following rules:

(i) The electronic configuration of an atom is built up from that of the element preceding it in the Periodic Table by adding one proton, an extranuclear electron and an appropriate number of neutrons.

(ii) The orbitals are successively filled in order of their increasing energy, the lowest energy available orbital being filled up first (aufbau principle). With the help of the *energy level diagram* (Fig. 1.9), it is possible to know the sequence in which the orbitals are filled up.

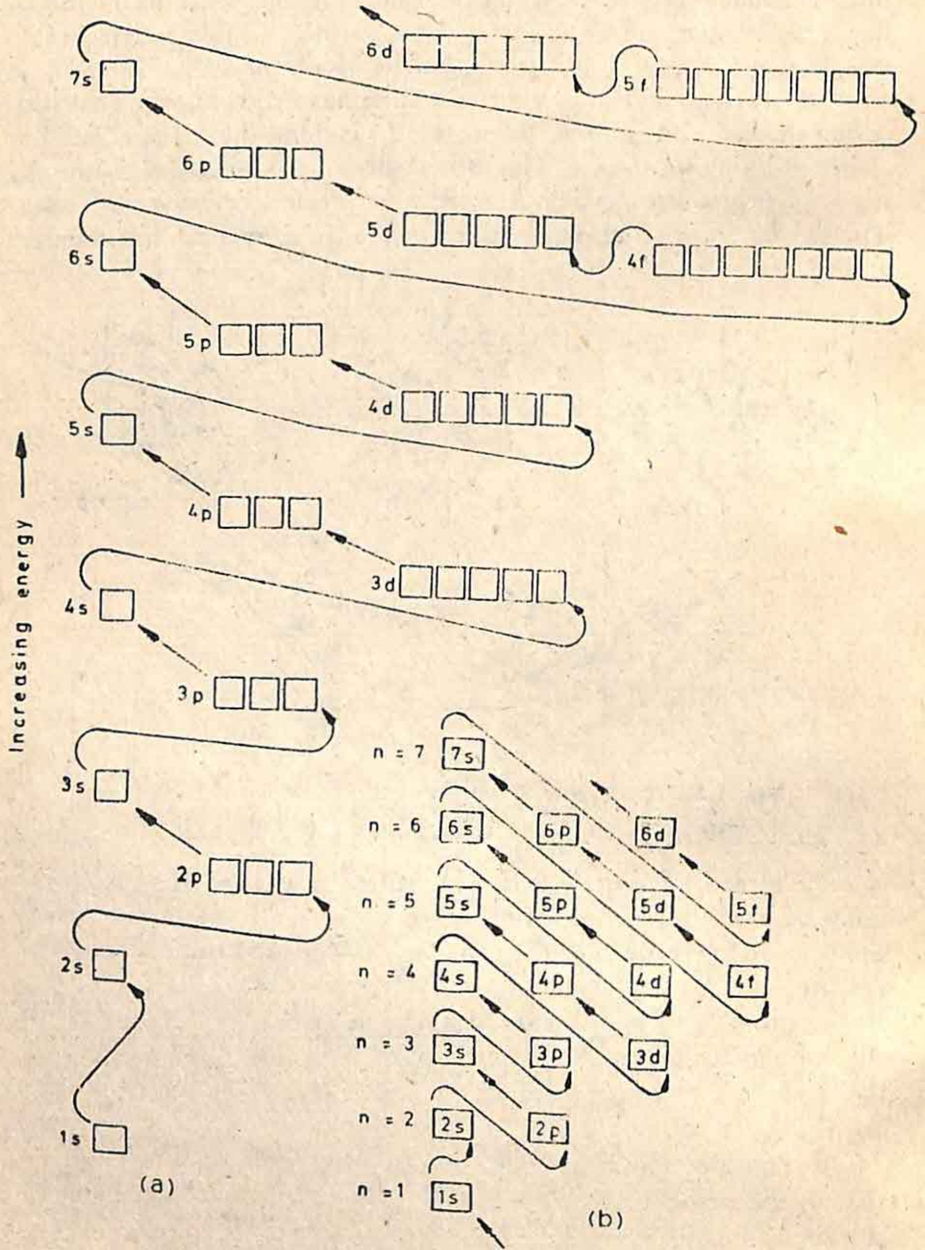


Fig. 1.9. Order of filling subshells in the building-up of electronic configurations. (a) Relative energies of various orbitals in atoms. (b) Aid to remember the order of filling subshells.

(iii) A single orbital cannot have more than two electrons. When two electrons occupy the same orbital they must have opposite spins (Pauli's exclusion principle).

(iv) Electron pairing in any orbital does not take place until all the available orbitals of a given set contain one electron each (Hund's rule of maximum multiplicity).

Keeping in view the above rules, let us write the electronic configurations of some atoms. In the following representation, an orbital is shown by a square box. An empty box means a vacant orbital, a box with an arrow shows a single electron in the orbital (half-filled orbital) and a box with two arrows with heads in reverse direction (↑ ↓) represents an orbital with two electrons (completely-filled orbital).

Hydrogen. There being only one electron in the hydrogen atom, it occupies 1*s* orbital. Thus, the configuration can be written as (Fig. 1.10).

H $1s^1$

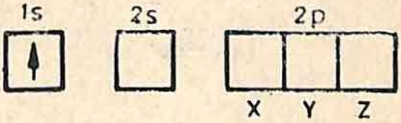


Fig. 1.10.

Helium. It has two electrons. Both occupy 1*s* orbital so as to fill it completely and they will have opposite spins (Fig. 1.11).

He $1s^2$

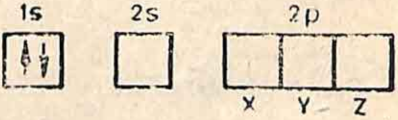


Fig. 1.11.

Lithium. It has three electrons. Since 1*s* electron cannot have more than two electrons, third electron moves to the next energy level, 2*s* (Fig. 1.12).

Li $1s^2\ 2s^1$

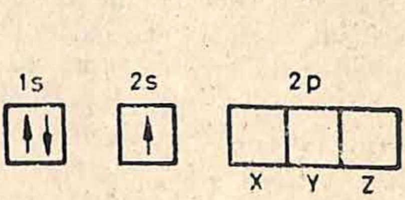


Fig. 1.12.

Beryllium. The fourth electron will occupy the $2s$ orbital to fill it completely (Fig 1.13).

Be $1s^2\ 2s^2$

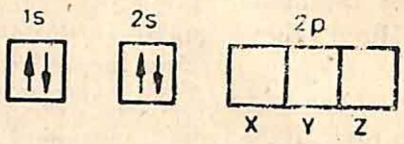


Fig. 1.13.

Boron. The fifth electron goes to one of the three $2p$ orbitals (p_x, p_y or p_z) with up or down orientation. Let us keep it in $2p_x$ with up orientation (Fig. 1.14).

B $1s^2 2s^2 2p^1$

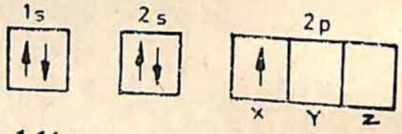


Fig. 1.14.

Carbon. The sixth electron will go to $2p_y$ or $2p_z$ orbital since $2p_x$ is already half-filled (Hund's rule) (Fig. 1.15).

C $1s^2 2s^2 2p^2$

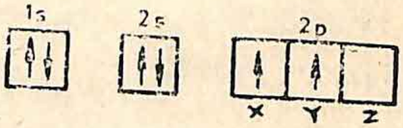


Fig. 1.15.

With similar reasoning, we can write the electronic configurations of the next twelve elements, viz., nitrogen, oxygen, fluorine, neon, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine and argon. It may be noted that in reaching neon, the K and L energy shells ($n=1$ and $n=2$) become fully occupied. In writing the electronic configurations of the subsequent elements, it is not necessary to write the completely filled K and L shells. Only the M shell (valence shell) orbitals may be represented (Fig. 1.16).

N	$1s^2 2s^2 2p^5$
O	$1s^2 2s^2 2p^4$
F	$1s^2 2s^2 2p^5$
Ne	$1s^2 2s^2 2p^6$
Na	$3s^1$
Mg	$3s^2$
Al	$3s^3 3p$
Si	$3s^2 3p^2$
P	$3s^2 3p^3$
S	$3s^2 3p^4$
Cl	$3s^2 3p^5$
Ar	$3s^2 3p^6$

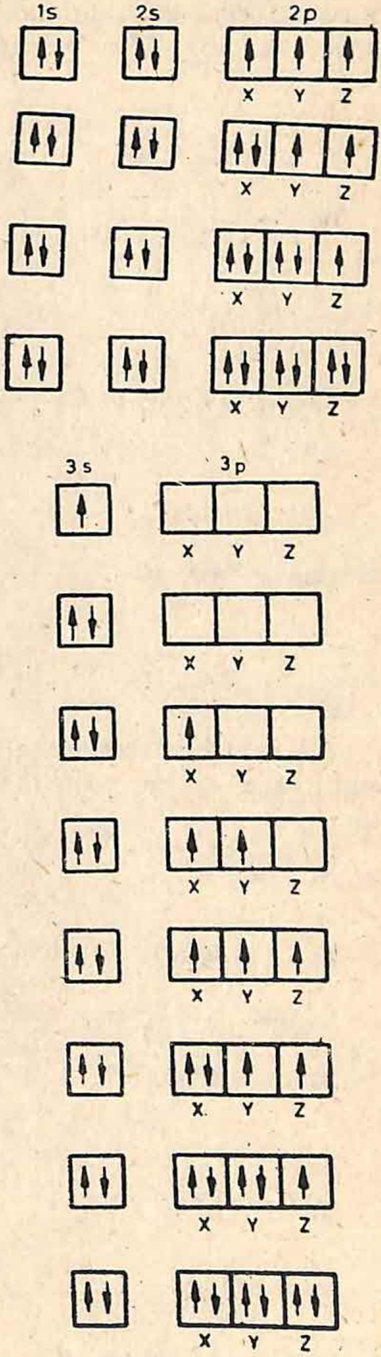


Fig. 1.16.

In the next element potassium, $3p$ orbital is followed by $4s$ and not $3d$ because $4s$ has lower energy as compared with $3d$ (energy level diagram). Thus, we can write potassium as :

K $4s^1$

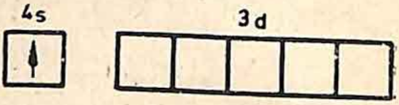


Fig. 1.17.

This is followed by Ca :

Ca $4s^2$

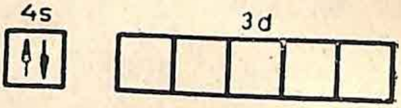


Fig. 1.18.

The next available orbital to $4s$ is $3d$ (energy level diagram) and hence we can write the configurations of subsequent elements as :

Sc $4s^2 3d^1$

Ti $4s^2 3d^2$

V $4s^2 3d^3$

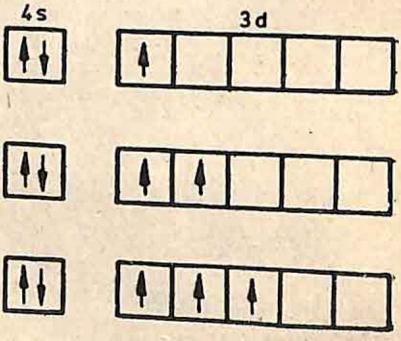
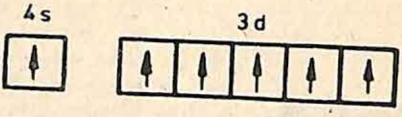


Fig. 1.19.

The configuration of the next element chromium should have been $4s^2 3d^4$ but it is actually $4s^1 3d^5$. This is because the electronci configurations having all the five *d* orbitals either completely half-filled or completely filled have extra stability.

Cr $4s^13d^5$



This is followed by :

Mn $4s^23d^5$

Fe $4s^23d^6$

Co $4s^23d^7$

Ni $4s^23d^8$

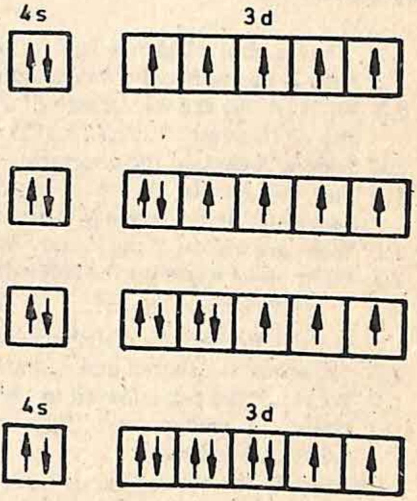


Fig. 1.20.

Again, the configuration of copper is $4s^13d^{10}$ though we should have expected it to be $4s^23d^9$. This is because of the extra stability of the completely filled five *d* orbitals.

Cu $4s^13d^{10}$

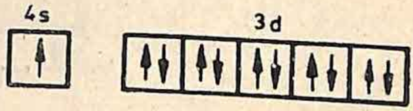


Fig. 1.21.

The next element zinc will be written as :

Zn $4s^23d^{10}$

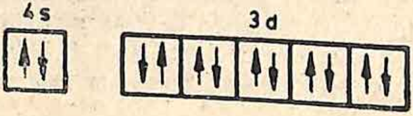


Fig. 1.22.

The electronic configurations of the rest of the elements of the Periodic Table can be written following the same rules as we have applied in the above elements.

EXERCISES

1.1 What is photoelectric effect? How is it explained?
1.2 How is the de Broglie wavelength related to momentum of a particle?
1.3 What will be the wavelength of a body of mass 2 mg moving with a velocity of 10 m sec^{-1}? (Ans. 3.3125×10^{-29} m)
1.4 State and explain the unceraint principle.
1.5 The uncertainty in the momentum of a particle is 3×10^{-2} kg m sec^{-1}. Calculate the uncertainty in its position. (Ans. 1.76×10^{-32} m)
1.6 What are quantum numbers? What do they signify?
1.7 Write short notes on the following:
    (*i*) Orbit and orbital (*ii*) Pauli's exclusion principle
    (*iii*) Probability distribution curves.
1.8 Represent the shapes and orientations of three *p* orbitals.
1.9 What are the rules obeyed in filling the electrons in various energy levels?
1.10 Draw the energy level diagram which shows relative energies of various orbitals in atoms.
1.11 Identify the atoms having the following configurations: (Fig. E 1.1)

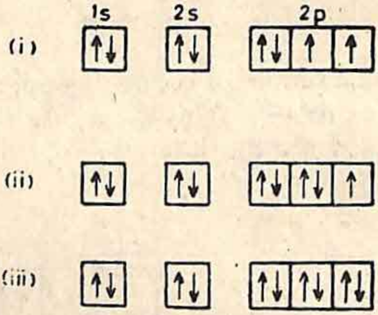


Fig. E 1.I.

1.12 Write the electronic configurations of elements with atomic numbers 8, 19, 27 and 35.
1.13 The uncertainty in the position of a moving bullet of mass 20 g is $\pm 1.0 \times 10^{-5}$ m. Calculate the uncertainty in its velocity. (Ans. 2.6×10^{-28} m sec^{-1})
1.14 Is it possible to determine both position and velocity of small moving particles like electrons? Explain.
1.15 Name the scientists who gave the relationships:

$$(i)\ \Delta p \times \Delta x \geqslant \frac{h}{4\pi}$$

$$(ii)\ E = h\nu$$

$$(iii)\ \lambda = \frac{h}{mv}$$

Explain their significance.

1.16. Explain why:

(*i*) Cr has the outer configuration $4s^1 3d^5$ and not $4s^2 3d^4$

(*ii*) Cu has the outer configuration $4s^1 3d^{10}$ and not $4s^1 3d^9$

(*iii*) K has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ and not $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

S.C.E.R.T. W.B. LIBRARY
Date 10.8.98
Accn. No. 9680

S.C.E.R.T. West Bengal
Library
25/3, B.C. Road
Calcutta

Unit 2

More about Molecules

Idea of molecular orbitals, bonding picture in simple molecules, hybridization.

In the previous class we have used the chemical bond approach or its modified version called valence bond (v.b.) approach to explain the bond formation of simple molecules. The presence of singly-occupied orbitals in different atoms and the two electrons occupying these separate orbitals having opposite spins are the necessary requirements to explain the bond formation with that approach. Under these two conditions, an overlap of orbitals takes place leading to a sharing of two electrons of opposite spins between the nuclei. This approach pertains to the part played by valence electrons in forming chemical bond and hence is known as valence bond method. It was mainly developed and advanced by Linus Pauling around 1930.

2.1 MOLECULAR ORBITAL METHOD

This is an another approach to explain chemical bonding and has been developed mainly by Robert Mulliken. Molecular orbital (m.o.) approach is more modern and explains the formation of a covalent bond in a better and more rational way. According to this approach, a molecule is considered to be different from the atoms from which it is formed. All the electrons belonging to both the atoms are considered to be moving along the entire molecule under the influence of all the nuclei.

Just as an atom has quantized atomic orbitals of varying energy levels, a molecule according to molecular orbital theory is believed to have quantized molecular orbitals which surround all the concerned nuclei in the molecule. The various electrons in the molecule are believed to occupy the various orbitals. Accordingly, any electron is believed to be associated with all the nuclei.

Similar to atomic orbital, a molecular orbital can be pictured as a charged cloud embracing all the nuclei. To minimize electron-electron repulsion, the two electrons in a molecular orbital at any moment are most probably as far from each other as possible while still remaining in the proximity of the nuclei. One essential difference between an atomic orbital and a molecular orbital is that while an electron in an atomic orbital is influenced by one positive nucleus, an electron in a molecular orbital is influenced by all the nuclei.

The molecular orbitals are devised in the same way as the atomic orbitals following the aufbau and Pauli exclusion principles. Thus a molecular orbital, like an atomic orbital, can contain the maximum number of two electrons which have opposite spins.

Let us appreciate the difference between the v.b. and m.o. theories considering the formation of hydrogen molecule by the combination of two hydrogen atoms. According to the v.b. theory, the two hydrogen atoms lie close together and the electron shell of each atom remains the same as in an isolated atom except that for part of the time, each shell contains two electrons instead of one in the isolated atom. The m.o. theory suggests that the hydrogen molecule consists of two nuclei lying at an appropriate distance from each other and the two electrons are located in one particular orbital called molecular orbital which is associated with the energy characteristic of the molecule. It must be remembered that molecular orbitals are quite different from atomic orbitals on account of their change in electric field due to the presence of two or more nuclei instead of one.

Linear combination of atomic orbitals

The most convenient way of working out the wave functions for molecular orbitals is to adopt the method of *linear combination of atomic orbitals* (LCAO). Let us consider two similar atoms 1 and 2 which have atomic orbitals described by the wave functions $\psi(1)$ and $\psi(2)$. When these two atoms form a bond, the electrons originally present in atomic orbitals now occupy molecular orbitals. The molecular orbital is formed by a linear combination of the atomic orbitals $\psi(1)$ and $\psi(2)$:

$$\psi = \psi(1) + \psi(2) \tag{2.1}$$

where ψ is the molecular orbital obtained by the combination of atomic orbitals $\psi(1)$ and $\psi(2)$.

In a diatomic molecule, the molecular orbital for an electron, in the field of nuclei 1 and 2, will be given by two modes of combinations:

$$\psi b=\psi(1)+\psi(2) \quad \text{(Bonding or symmetric)} \qquad (2.2)$$

$$\psi a=\psi(1)-\psi(2) \quad \text{(Antibonding or antisymmetric)} \qquad (2.3)$$

The probability of finding the electrons in the molecular orbital obtained by linear combination, according to equation (2.2), is greater than that in either of the atomic orbitals $\psi(1)$ and $\psi(2)$. The new orbital is called a *bonding molecular orbital*. On the other hand, the probability of finding electrons in the molecular orbital by the LCAO, in accordance with equation (2.3), is less than that in either of the atomic orbitals $\psi(1)$ and $\psi(2)$. The new orbital is called an *antibonding molecular orbital*.

Since an electron in an antibonding molecular orbital cancels out the stability brought in by the electron in the bonding molecular orbital. Therefore for bonding to occur, there should be an excess of bonding electrons over the antibonding electrons. In case, the number of bonding electrons is equal to that of antibonding electrons, no bond will be formed between the atoms. The ***number of bonds*** or ***bond order*** in a molecule may be defined as half of the difference between numbers of electrons in bonding (N_b) and antibonding (N_a) orbitals.

$$\text{Bond order (b.o.)}=\tfrac{1}{2}(N_b-N_a)$$

The formation of bonding molecular orbital (ψ_b) and that of antibonding molecular orbital (ψ_a) from two atomic orbitals $\psi(1)$ and $\psi(2)$ is shown (Fig. 2.1.) The bonding m.o. has a lower energy than that either of the atomic orbitals whereas the antibonding m. o. has higher energy than that either of the atomic orbitals.

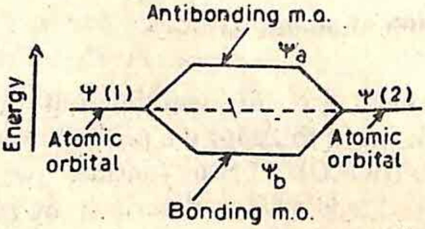


Fig. 2.1. Formation of bonding and antibonding molecular orbitals.

Combination of *s-s* Orbitals

Let us take the simple case of combination of 1*s* orbital of one hydrogen atoms with 1*s* orbital of another hydrogen atom to give two molecular orbitals in a hydrogen molecule. Considering the wave nature of electrons, there are two ways of combining the atomic orbitals—addition and subtraction. If these are combined by addition, the boundary surface of the resulting molecule will be as shown in Fig. 2.2.

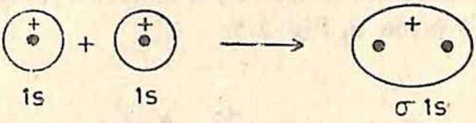


Fig. 2.2. The boundary surface of σ 1*s* molecular orbital formed by two 1*s* atomic orbitals.

The orbitals may be represented in terms of charge clouds as shown in Fig. 2.3.

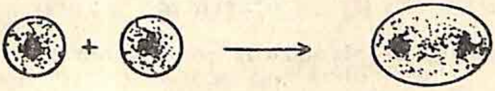


Fig. 2.3. Two 1*s* atomic orbitals and the resulting σ 1*s* molecular orbital represented in terms of charge clouds.

This shows that there is an accumulation of negative charge between the nuclei. It is this which holds the nuclei together at an equilibrium internuclear distance and which constitutes the covalent bond previously denoted by H-H. This molecular orbital is said to be a bonding molecular orbital, denoted by σ1*s*, σ because it is cylindrically symmetrical about the molecular axis, and 1*s* because it is formed by the combination of 1*s* atomic orbitals. The bond formed between two atoms by a σ molecular orbital is called a *σ bond*.

The second way of combining two orbitals is by subtraction, the two electron waves cancel each other since they are oriented in opposite directions. Thus there is practically no possiblity of finding electrons in the region of overlap. As the negative charge is withdrawn from the region between the nuclei, the repulsive force increases between them (Fig. 2.4). This molecular orbital is called an antibonding molecular orbital and is labelled as σ* 1*s*. Antibonding orbitals are marked with asterisks (*).

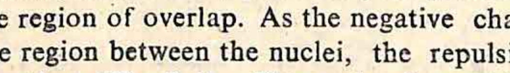


Fig. 2.4 Formation of antibonding σ*1*s* molecular orbital by subtraction.

A combination of two atomic orbitals must give two molecular orbitals to accommodate the available electrons. Each atomic orbital and each molecular orbital can contain a maximum of two electrons with opposite spins. One of the molecular orbitals is bonding and the other is antibonding.

Keeping in view the above information of bonding and antibonding molecular orbitals, hydrogen molecule may be represented graphically as given in Fig. 2.5.

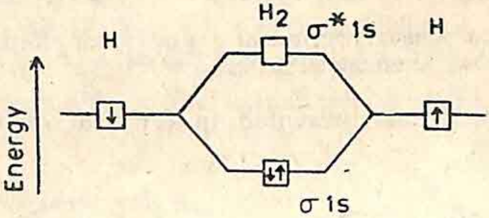


Fig. 2.5. Formation of $\sigma 1s$ and σ^*1s molecular orbitals in H_2 molecule.

Combination of s-p orbitals

An *s* orbital combines with a *p* orbital when the lobes of the *p* orbital are pointing along the axis joining the nuclei. A bonding molecular orbital results when the adjacent lobes have the same sign. This orbital is represented as *σsp*. The corresponding antibonding molecular orbital is formed when the adjacent lobes are of opposite sign. It is represented as *σ*sp*.

Combination of p-p orbitals

If we consider two *p* orbitals (say $2p_z$) having their lobes pointing along the axis joining the nuclei (*z*—axis), we will obtain $\sigma 2p_z$ and $\sigma^* 2p_z$ molecular orbitals as in Fig. 2.6.

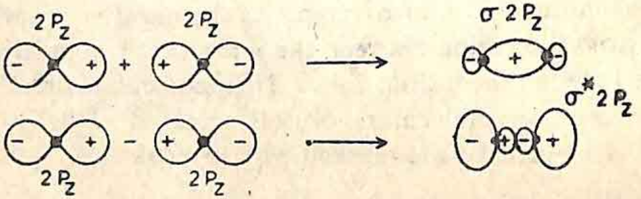


Fig. 2.6. Formation of $\sigma 2p_z$ and σ^*2p_z molecular orbitals by combination of $2p_z$ atomic orbitals.

In case of combination of two *p* orbitals (say $2p_x$ or $2p_y$) having lobes perpendicular to the axis joining the nuclei, lateral overlap of orbitals will take place. This results in forming π bonding and π* antibonding molecular orbitals (Fig. 2.7).

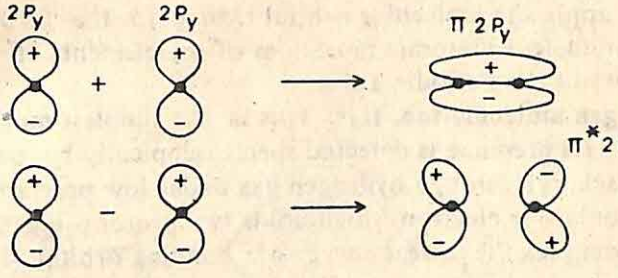


Fig. 2.7. Formation of $\pi 2p_y$ and $\pi^* 2p_y$ molecular orbitals by addition and subtraction overlap of $2p_y$ atomic orbitals.

2.2. STRUCTURES OF SIMPLE DIATOMIC MOLECULES

The order of increasing energy for molecular orbitals has been determined from spectroscopic measurements. It is clearly depicted in Fig. 2.8. This sequence helps to work up the electronic structures of simple diatomic molecules. The other guidelines are:

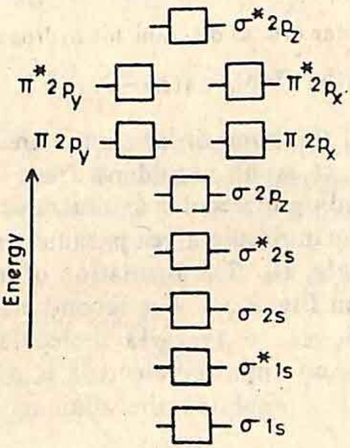


Fig. 2.8. Energy levels for filling molecular orbitals for diatomic homonuclear molecules.

(i) The molecular orbitals of lowest energy are filled up first (aufbau principle).

(ii) The maximum number of electrons in a molecular orbital is two (Pauli's exclusion principle).

(iii) Pairing of electrons takes place when each molecular orbital of the same energy has at least one electron. It means whenever two equal energy molecular orbitals are available, electrons prefer to remain unpaired (Hund's rule).

Let us apply the molecular orbital theory to the formation of some homonuclear diatomic molecules of the elements of first and second rows of the Periodic Table.

Hydrogen molecule-ion, H_2^+. This is the simplest molecule that can exist. Its presence is detected spectroscopically by passing an electric discharge through hydrogen gas under low pressure.

It has only one electron which holds two protons together. This electron occupies the lowest energy $\sigma 1s$ bonding orbital (Fig. 2.9).

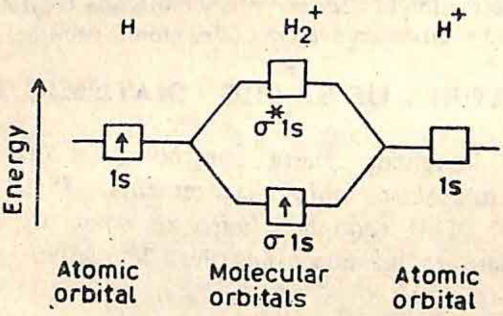


Fig. 2.9. Molecular orbital diagram for hydrogen molecule-ion.

$$\text{Bond order (b.o.)} = \tfrac{1}{2}(N_b - N_a) = \tfrac{1}{2}(1-0) = \tfrac{1}{2}$$

The positive value of the bond order means that the molecule-ion has some stability. It is also evident from this that the lone electron is in a bonding molecular orbital. Because of the presence of a lone electron, the molecule gives paramagnetic properties.

Hydrogen molecule, H_2. The formation of hydrogen molecule is already represented in Fig. 2.5. The second electron of this two-electron molecule moves to the $\sigma 1s$ molecular orbital but with opposite spin. Since no unpaired electron is present in any of its molecular orbitals, it explains the diamagnetism of molecular hydrogen.

The value of the bond order $[=\tfrac{1}{2}(2-0)=1]$ shows that two hydrogen atoms are connected by a single bond in the molecule. The positive value indicates that the molecule is stable. The values for bond energy and bond length are found to be 433 kJ mol^{-1} and 0.74×10^{-10}m, respectively.

Helium molecule-ion, He_2^+. It has three available electrons—two of which occupy a $\sigma 1s$ bonding orbital and the third one moves to the σ^*1s antibonding orbital (Fig. 2.10). The He_2^+ molecule-ion has been detected in a discharge tube. Its bond order $[=\frac{1}{2}(2-1)=\frac{1}{2}]$ being the same as in H_2^+, the dissociation energies and bond lengths of the two molecule-ions are comparable. The presence of an unpaired electron in the σ^*1s antibonding orbital imparts paramagnetism to the molecule.

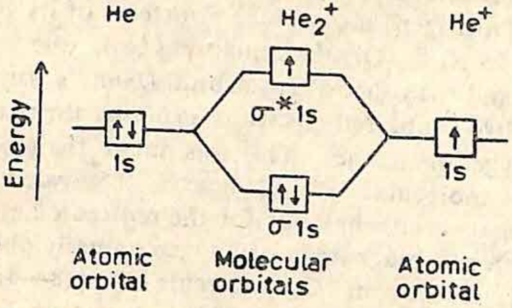


Fig. 2.10. Molecular orbital diagram for helium molecule-ion.

Hypothetical helium molecule, He_2. The fourth electron will also move to σ^*1s antibonding orbital making the bond order, $\frac{1}{2}(2-2)=0$ (Fig. 2.11). The value of bond order suggests that such a molecule cannot exist and there is no evidence available for its existence.

Let us now consider some more important diatomic molecules like nitrogen, oxygen and fluorine.

Nitrogen molecule, N_2. The electronic configuration of nitrogen atom is $1s^2$, $2s^2$, $2p^3$. So there are fourteen electrons in the diatomic molecule which are accommodated in the seven lowest energy orbitals, $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $\sigma 2p_z$, $\pi 2p_x$ and $\pi 2p_y$ (see energy level diagram, Fig. 2.8). Of these, 10 electrons are present in 5 bond-

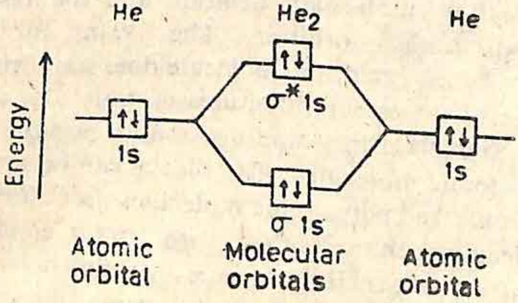


Fig. 2.11. Molecular orbital diagram for hypothetical He_2 molecule.

ing orbitals and 4 in 2 antibonding orbitals. Therefore, the bond order$=\frac{1}{2}$ (10—4 =3. This shows that the molecule is triply bonded as N≡N. It is also deduced that it must have a very high dissociation energy. In fact, the value obtained for dissociation energy of the molecule (945 kJ mol^{-1}) is the highest amongst the diatomic molecules. The absence of an unpaired electron in any of the molecular orbitals imparts diamagnetic character to the molecule.

Oxygen molecule, O_2. Oxygen molecule contains 2 more electrons than the nitrogen molecule. Fourteen of its 16 electrons are distributed as in N_2. Of the remaining two, one will be assigned π^*2p_y orbital and the other π^*2p_x orbital (Hund's rule). Thus the presence of two unpaired electrons explains the paramagnetic behaviour of oxygen molecule. This was one of the greatest achievements of the molecular orbital theory. The valence bond theory predicted diamagnetic behaviour for the molecule and it failed to account for the paramagnetism of oxygen actually observed.

The bond order in O_2 molecule is $\frac{1}{2}$(8—4)=2, showing that the two oxygen atoms in the molecule are connected by a double bond. The value obtained for dissociation energy (495 kJ mol^{-1}) supports the expectation.

Fluorine molecule, F_2. It has two more electrons than the oxygen molecule making a total of 18 electrons. These two additional electrons occupy the half-filled π^*2p_y and π^*2p_x orbitals. Thus in a F_2 molecule, we have 10 bonding and 8 antibonding electrons giving a value of $\frac{1}{2}$(10—8)=1, for the bond order. It shows that there is a single bond in the molecule. All the electrons in bonding and antibonding molecular orbitals are paired, hence it shows the expected diamagnetism.

Neon molecule, Ne_2. It contains two more electrons than fluorine and these occupy σ^*2p_z orbital. Of the 20 electrons, half occupy 5 bonding molecular orbitals and the rest occupy 5 antibonding molecular orbitals. The value for bond order is $\frac{1}{2}$(10—10)=0. As expected, the molecule does not exist.

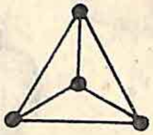
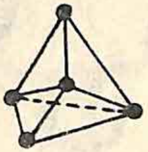
We have learnt the essential features of molecular orbital theory and applied it to explain the bonding and molecular behaviour of homouclear diatomic molecules. The theory can be applied to heteronuclear diatomic and polyatomic molecules. Both the valence bond as well as molecular orbital methods are useful in explaining the bonding in molecules. Certain properties of molecules can be easily explained by valence bond method while molecular orbital method becomes more suitable in other cases. Both theories satisfactorily explain the characteristics of almost all compounds.

2.3 HYBRIDIZATION

In class XI we have learnt sp, sp^2 and sp^3 types of hybridization. The concept was used to explain the nature of compounds formed by beryllium, boron and carbon. In all these cases, the hybridization involved s and p orbitals. The characteristics of the resulting hybrid orbitals are summarized in Table 2.1.

In this section, we shall learn two other types of hybridization, viz., sp^3d (or trigonal bipyramidal) and sp^3d^2 (or octahedral).

TABLE 2.1 : Characteristics of Hybrid Orbitals

Hybridization	*No. of hybridized orbitals*	*Bond angle*	*Shape*	*Examples*
sp	2	180°	Linear	BeF_2, C_2H_2
sp^2	3	120°	Plane triangle 	BF_3, C_2H_4
sp^3	4	109°28′	Tetrahedron 	CH_4

sp^3d Hybridization

Let us consider the gaseous molecule PF_5 or PCl_5. The central phosphorus atom has only three unpaired electrons in its electronic configuration. In order to explain the formation of the pentavalent molecule, one of the $3s$ electrons is excited or promoted to the vacant $3d$ orbital. This results in sp^3d hybridization (Fig. 2.12) and gives rise to a trigonal bipyramidal structure (Fig. 2.13). It should

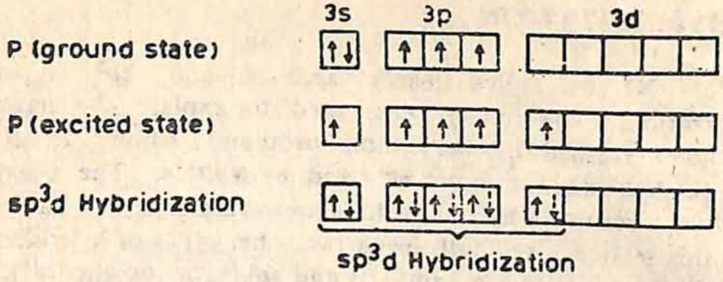
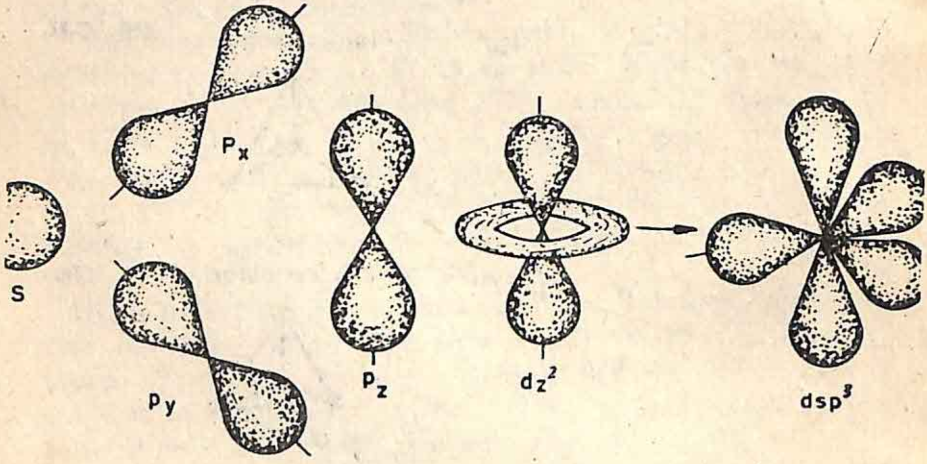


Fig. 2.12. Formation of PX_5 molecule by sp^3d hybridization.

be remembered that the concept of hybridization is invoked only between orbitals of approximately the same energy. All the five hybrid orbitals are not equivalent. One set of three coplanar equivalent sp^2 orbitals is directed towards the corners of an equilateral triangle while the other consisting of two equivalent *dp* orbitals is perpendicular to the plane of the triangle, above and below it. This picture is in conformity with the experimentally determined structure of the molecule.



2.13. Formation of a trigonal pyramidal structure by sp^3d hybridization.

sp^3d^2 Hybridization.

Let us consider sulphur hexafluoride molecule. Two electrons (one from 3*s* orbital and one from 3*p* orbital) of sulphur atom are promoted to two 3*d* orbitals. Now there are six orbitals singly occupied which hybridize to give a set of six sp^3d^2 hybridized orbitals (Fig. 2.14) directed towards the corners of a regular octahedron. This explains the octahedral structure of sulphur hexafluoride

(Fig. 2.15). The characteristics of sp^3d, sp^3d^2 and also dsp^2 (square planar) hybrid orbitals are given in Table 2.2.

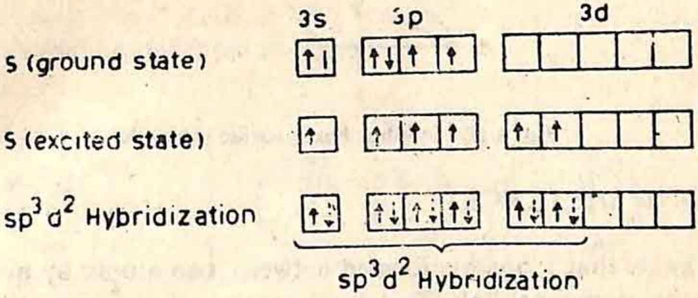
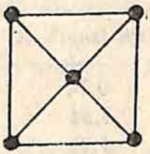
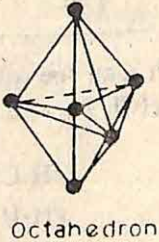
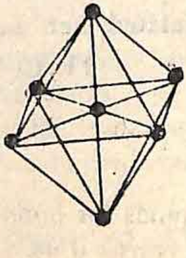


Fig. 2.14. Formation of SF$_6$ molecule by sp^3d^2 hybridization.

TABLE 2.2 : Characteristics of dsp^2, sp^3d and sp^3d^2 hybrid orbitals

Hybridization	*No. of outer orbitals*	*Bond angle*	*Shape*	*Examples*
dsp^2	4	90°	Square plannar 	[Ni(CN)$_4$]$^{2-}$, [PtCl$_4$]$^{2-}$
sp^3d	5	90°, 120°	Trigonal bipyramid 	PF$_5$, PCl$_5$
op^3d^2	6	90°	Octahedron 	SF$^+_6$, [Co(NH$_3$)$_6$]$^{+3}$

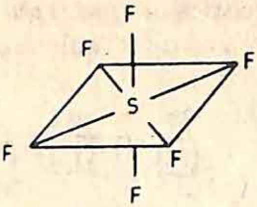


Fig. 2.15 Sulphur hexafluoride molecule.

2.4. BOND DISTANCE

We know that a bond is formed between two atoms by overlapping of the atomic orbitals. This overlap occurs only at a certain distance where the potential energy is minimum. The average equilibrium distance between the centres of nuclei of two bonded atoms is known as *bond distance* or *bond length*. It is expressed in Å. The average bond distances of some bonds in molecules are given in Table 2.3. The actual bond distance between two atoms depends on the nature of the atoms, the nature of the bond between them and other factors.

TABLE 2.3 : Some Bond Lengths

Bond	*Bond length,* Å	*Bond*	*Bond length,* Å
H-H	0.74	H-Cl	1.36
C-C	1.54	C-H	1.09
Cl-Cl	1.98	C-Cl	1.77
C=C	1.33	O-Cl	0.96
C≡C	1.20	C-O	1.42

Bond length can be obtained experimentally. Let us consider the molecules HCl, H_2 and Cl_2. The bond lengths in these molecules are:

$$\bar{r}\text{H-Cl} = 1.36\ \text{Å}$$

$$\bar{r}\text{H-H} = 0.74\ \text{Å}$$

$$\bar{r}\text{Cl-Cl} = 1.98\ \text{Å}$$

It can be calculated that

$$\bar{r}\text{H-Cl} = \tfrac{1}{2}(r\text{H—H}) + \tfrac{1}{2}(r\text{Cl-Cl})$$

$$= \frac{0.74}{2} + \frac{1.98}{2}$$

$$= 0.37 + 0.99 = 1.36\ \text{Å}$$

(where *r* stands for bond length)

This equation is true if we assume that the atoms are in contact in a molecule. The radius of the hydrogen atom (covalent radius) will be half of the bond distance in H_2. Similarly the covalent radius of chlorine atom will also be half the bond length in Cl_2. This is thus clear that HCl bond length is the sum of the covalent radii of the two atoms. This is depicted in fig. 2.16.

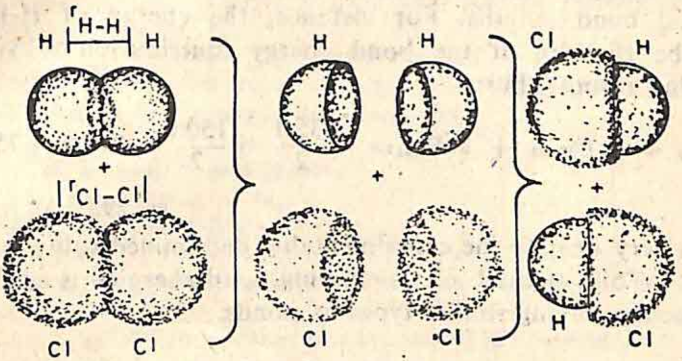


Fig 2.16 Formation of two HCl molecules from combination of one hydrogen molecule and one chlorine molecule.

Covalent radius changes depending on the multiplicity of the bonds between atoms. It has a higher value for a single bond and it decreases for a double bond (by obout 14%) and for a triple bond (by about 22%). Table 2.4 gives single and multiple covalent bond radii of some atoms.

TABLE 2.4 : Single and Multiple Covalent Bond Radii of Some Atoms

Single bond radii, Å								*Multiple bond radii, Å*	
H	0.37	N	0.70	O	0.66	F	0.64	C=	0.67
C	0.77	P	1.10	S	1.04	Cl	0.99	C≡	0.61
Si	1.17	As	1.21	Se	1.17	Br	1.14	N≡	0.55
Ge	1.22	Sb	1.41	Te	1.37	I	1.33		

2.5. BOND ENERGY

The amount of energy required to break one mole of the bonds and separate the bonded atoms in the gaseous state is known as *bond energy*. It is a measure of the strengh of the bond.

For a diatomic molecule like hydrogen, the bond energy is the same as the bond dissociation energy since the breaking of one bond disrupts the whole molecule.

$H_2\,(g) \longrightarrow 2H\,(g)$ Bond energy= $+435.1$ kJ mol^{-1}

For polyatomic molecules, the bond energy is not equal to bond dissociation energy. For example, in molecule like NH_3, the N-H bond energy is one-third of the energy to dissociate NH_3 molecule into atoms. The single bond energies of some common bonds are given in Table 2.5.

Bond energies can be calculated in the same way as we have calculated bond lengths. For instance, the energy of H-I bond should be the sum of the bond energy contribution of hydrogen and iodine atoms. Thus:

$$E_{H-I} = \tfrac{1}{2} E_{H-H} + \tfrac{1}{2} E_{I-I} = \frac{435.1}{2} + \frac{150.6}{2} = 217.7 + 75.3$$
$$= 293.0 \text{ kJ mol}^{-1}$$

which is very near to the experimentally determined value of 297 kJ mol^{-1}. This method of calculating bond energies is applicable for molecules having similar types of bonds.

TABLE 2.5 : Energies of Some Common Bonds

Bond	*Bond energy,* kJ mol^{-1}	*Bond*	*Bond energy,* kJ mol^{-1}
H-H	435.1	O-O	138.1
H-F	564.8	S-S	263.6
H-Cl	431.0	C-O	351.5
H-Br	364.0	C-H	414.2
H-I	297.1	C-C	347.3
F-F	154.8	C=C	619.2
Cl-Cl	242.7	C=O	707.1
Br-Br	192.5	N≡N	941.4
I-I	150.6	C≡N	878.6

EXERCISES

2.1 What is meant by m.o. approach? How does it differ from v.b. approach? Explain with an appropriate example.

2.2 What is meant by LCAO? Give the wave equation for bonding and antibonding moleculer orbitals.

2.3 Compare the following orbitals:
(i) Atomic and molecular
(ii) Bonding and antibonding
(iii) Sigma and pi.

2.4 Discuss briefly the combination of the following orbitals by addition and subtraction:

(i) *s-s* orbitals
(ii) *s-p* orbitals
(iii) *p-p* orbitals.

2.5 Give the energy sequence of molecular orbitals and depict the same by a diagram.

2.6 With the help of cell diagrams, explain the bonding in following molecules and molecule-ions:

(i) H_2 (ii) H_2^+ (iii) He_2^+ (iv) He_2

2.7 Explain the characteristics of oxygen, nitrogen and fluorine molecules applying the m.o. theory to their formation.

2.8 Explain why

(i) O_2 molecule is paramagnetic
(ii) N_2 molecule is diamagnetic
(iii) F_2 molecule is diamagnetic.

2.9 How does m.o. method explain non-existence of Ne_2?

2.10 What is meant by hybridization? What type of hybridization takes place in PCl_5 molecule?

2.11 Explain sp^3d^2 hybridization with the help of SF_6 molecule.

2.12 (a) Explain the terms:

(i) Bond length
(ii) Bond energy
(iii) Bond dissociation energy.

(b) The bond length of H-H and Cl-Cl molecules are 0 74 and 1.98 Å, respectively. Calculate the bond length of H-Cl. (Ans. 1 36 Å)

Unit 3

More about State of Matter

Solids, Bonding, Packing, Unit cells and crystal types, Defects in solids, Conduction in solids.

In class XI, we have studied some characteristics of solids and seen how they could be distinguished from liquids and gases. In this Unit, we shall study more about the state of matter and learn some aspects of crystalline state of solids.

3.1. CLASSIFICATION OF SOLIDS

All solids are characterized by *incompressibility, rigidity* and *mechanical strength.* This indicates that molecules, atoms or ions that make up a solid are closely packed, *i.e.*, they are held together by strong forces and cannot move at random. Thus in a solid, we have well-ordered molecular arrangement.

Solids may be broadly divided into two classes : (*i*) True solids and (*ii*) Pseudo solids.

True solids

They have definite shapes which they maintain against distorting forces.

Pseudo solids

They cannot stand against distorting forces and can be easily distorted by compressing and bending forces. They may even tend to flow slowly under their own weight and thus lose shape. Glass and pitch are two notable examples of such solids. You may have observed that window glasses of old buildings are thicker at the bottom and thinner at the top. These solids apparently look rigid and have a shape. They can be better described as *supercooled liquids*. Such solids do not melt sharply on heating as they gradually soften over a wide range of temperature and finally change into liquid state.

Solids may also be classified as : (*i*) Shapeless *amorphous* solids and (*ii*) well-shaped *crystalline* solids.

Amorphous solids. They include substances such as glass, fused silica, rubber and polymers of high molecular masses such as starch, cellulose, proteins, plastics, etc. Amorphous solids do not have any pattern or arrangement of molecules, atoms or ions, and, therefore do not have any definite geometrical shape. It has been found that even if some arrangement of the constituent units exists in a few amorphous solids, it does not extend to more than a few Å units. These crystalline parts of amorphous solids are called *crystallites*.

Crystalline solids. A crystalline solid has a definite and regular geometry due to definite and orderly arrangement of molecules, atoms or ions in a three-dimensional space. Crystalline solids may be classified according to the nature of particles constituting them and the binding forces between them (Table 3.1).

A crystalline substance can be distinguished by a simple method: Cut a crystalline solid with a sharp-edged knife. It will give a clean cleavage while an amorphous solid gives irregular fracture (Fig. 3 1.).

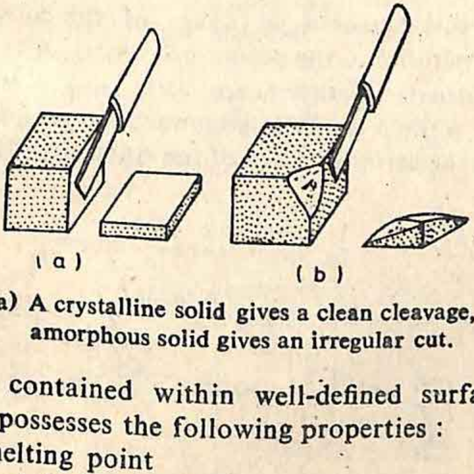


Fig. 3.1. (a) A crystalline solid gives a clean cleavage, (b) An amorphous solid gives an irregular cut.

A crystal is contained within well-defined surfaces known as *planes*. It also possesses the following properties :

(*i*) A sharp melting point

(*ii*) A characteristic heat of fusion

(*iii*) General incompressibility

(*iv*) A definite three-dimensional arrangement.

3.2 STUDY OF CRYSTALS BY X-RAYS

The study of the crystalline structure has been carried out by X-rays. The crystals act as diffraction gratings on interaction with X-rays. It has been shown that the units in the crystals are arranged in planes at close distances in a repeated manner. W. H. Bragg and his son W. L. Bragg studied the diffraction pattern of X-rays on ZnS crystal in order to locate the positions of Zn and S atoms. Later Debye, Scherrer and Hull used powdered substance in place of a single crystal. The diffraction pattern was taken on a circular film surrounding the powdered substance (Fig. 3.2). A simple illustration of apparatus employed for studying X-ray diffraction is shown in Fig. 3.3.

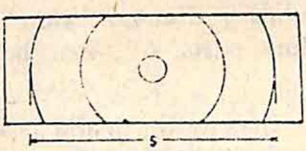


Fig 3.2. Typical X-ray diffraction pattern of the powder of a crystalline substance (Debye-Scherrer-Hull technique). The diameter S bears a direct relation with the dimensions of the unit cell.

Bragg gave an equation to study crystals. It is known as *Bragg's equation* :

$$n\lambda = 2d \sin \theta \tag{3.1}$$

where d is the distance between planes of the constituent particles of the crystal, parallel to the plane on which X-rays fall, 2θ is the angle of the diffracted X-ray beam (Fig. 3.4), λ is the wavelength of X-rays used while n is a whole number integer (1, 2, 3, . . ., etc.) which denotes the serial number of the diffracted beam.

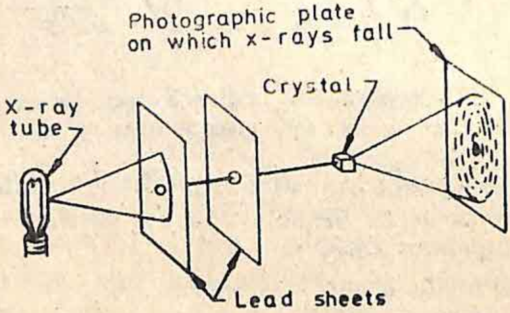


Fig. 3.3. A set-up for the study of X-ray diffraction pattern.

TABLE 3.1 : Types of Crystalline Solids

Crystalline solid	*Constituent particles*	*Binding forces*	*Physical properties*	*Examples*	*Approximate energy required to separate particles* (kJ mol^{-1})
Molecular	Molecules	van der Waals, dipole-dipole	Soft, low melting point, volatile, good insulator, low heat of fusion	Ar CH_4 Cl_2 CO_2	6.7 8.4 20.5 25.1
Ionic	Positive and negative ions	Coulombic electrostatic attraction	Quite hard, brittle, fairly high melting, point, insulating, high heat of fusion	NaCl NaF AgCl LiF	769.9 903.7 903.7 1033.5
Covalent	Atoms	Shared electrons	Very hard, very high melting point, non-conducting, high heat of fusion	Silicon Diamond	439.3 711.3
Metallic	Positive ions in a 'sea' of electrons	Electrical attraction	hard and soft, moderate to very high melting point, good conductor, malleable, ductile, moderate heat of fusion	Li Al Fe W	159.0 322.2 414.2 836.8

With equation (3.1), it is possible to calculate the distance d between repeating planes of particles of the crystal. Alternatively, knowing the distance between planes of known crystal, it is possible to calculate the wavelength of the X-ray used.

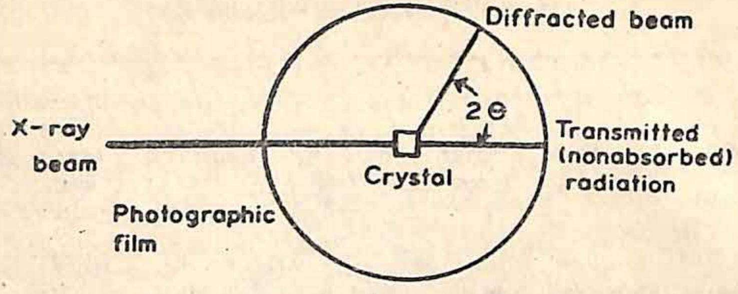


Fig. 3.4. A simple representation of X-ray diffraction.

Example 3.1- Calculate the wavelength of the X-rays when the diffraction angle 2θ is 16° for a crystal, the interplanar distance is 0.22 nm and only first order diffraction is seen.

Solution $n\lambda = 2d \sin \theta$ (Bragg's equation)

Now, $n = 1$, $2\theta = 16°$ and $d = 0.22$ nm

Putting the values, in the Bragg's equation:

$$\begin{aligned} 1 \times \lambda &= 2 \times 0.22 \times 10^{-9}\ \text{m} \times \sin 8° \\ &= 0.44 \times 10^{-9}\ \text{m} \times 0.139 \\ &= 0.0616 \times 10^{-9}\ \text{m} \\ &= 0.616\ \text{Å} \end{aligned}$$

3.3. SPACE LATTICE AND UNIT CELL

A *space lattice* (also called *crystal lattice*) means the regular arrangement of pattern of points (atoms, ions or molecules) in a three-dimensional space within a crystal. The lattice has to be thought of as extending in all directions through the entire crystal. The smallest portion of the space lattice (Fig. 3.5) which shows the pattern of the lattice is called *unit cell* (marked by bold lines in Fig. 3.5). Such unit cells are repeated over and over again in three

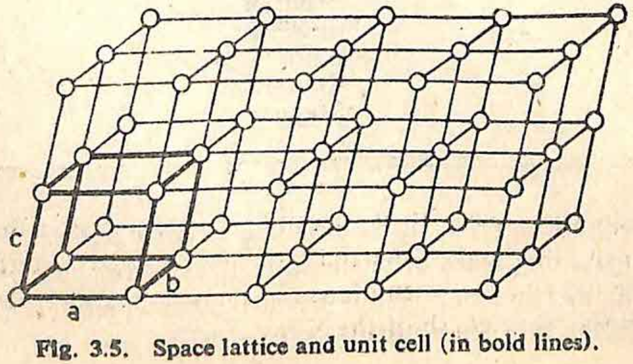
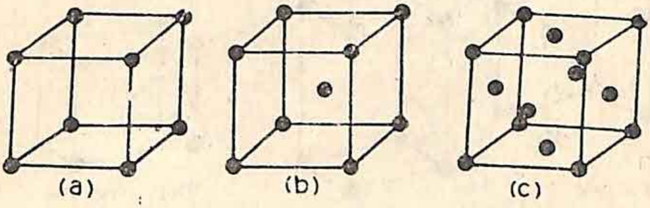


Fig. 3.5. Space lattice and unit cell (in bold lines).

dimension and result into the space lattice of the crystal. It is not possible for a single unit cell to exist alone since the boundaries of a unit cell are also the boundaries of the neighbouring unit cells. It may be noted that the *points* and not *lines* represent the space lattice. The lines drawn represent three axes which describe the relative positions of the points. In order to describe a unit cell, it is required to know the distances a, b and c, *i.e.*, the lengths of the edges of the unit cell, and the angles α, β and γ between the pair of edges (b, c), (c, a) and (a, b) respectively. For the cubic system of crystals, the following three different types of unit cells are known to exist (Fig. 3.6):



Simple or primitive cubic unit cell

Body centred cubic (bcc) unit cell

Face centred cubic (fcc) unit cell

Fig. 3.6. Types of unit cells for cubic system of crystals.

Simple or primitive

It is the arrangement in which the atoms, ions or molecules are present at the corners of the unit cell.

Body centred

In the arrangement, in addition to the points at the corners, there is one point at the centre within the unit cell.

Face centred

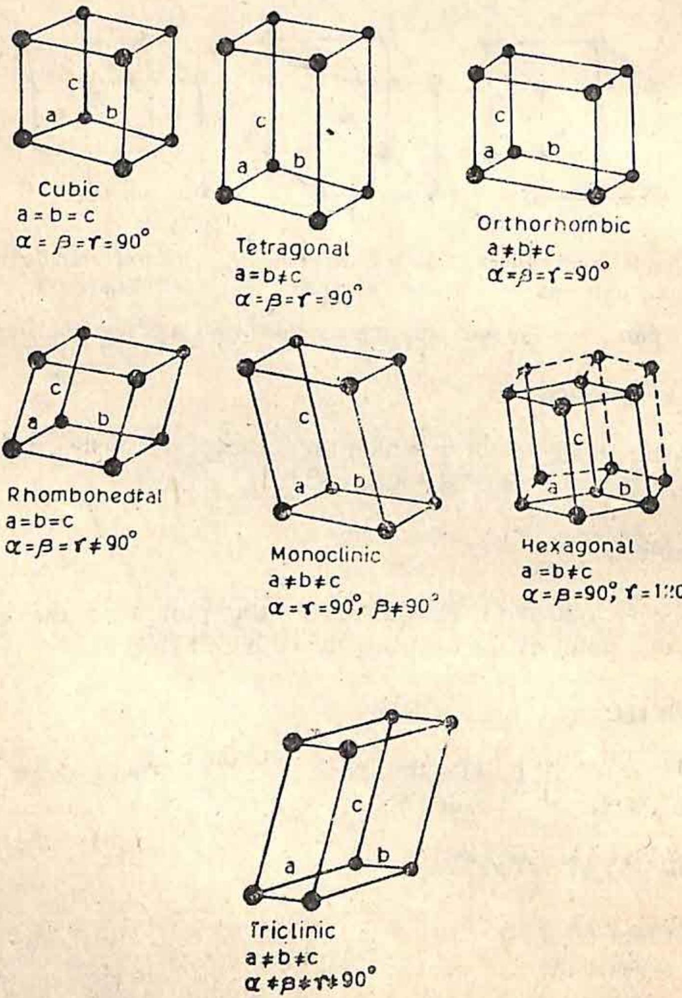
In the unit cell, besides the points at the corners there is one point in the centre of each face.

3.4. CRYSTAL SYSTEMS

Examination of a very large number of crystals of various substances reveals that only seven possible crystal types called *seven crystal systems* or *crystal habits* are found. These are shown in Fig. 3.7 and their characteristics are given in Table 3.2.

TABLE 3.2 : Seven Crystal Systems

Crystal system	*Axes*	*Axial angles*	*Examples*
Cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$	Copper, NaCl, zinc blended
Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$	White tin, SnO_2, TiO_2
Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$	Rhombic sulphur
Rhombohedral	$a=b=c$	$\alpha=\beta=\gamma\neq 90°$	Calcite ($CaCO_3$)
Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90°$; $\beta\neq 90°$	Monoclinic sulphur
Hexagonal	$a=b\neq c$	$\alpha=\beta=90°$; $\gamma=120°$	Graphite, ZnS, BN
Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$	Potassium dichromate



Cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$

Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

Monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90°$, $\beta \neq 90°$

Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°$, $\gamma = 120°$

Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

Fig. 3.7. Seven crystal systems.

3.5 PACKING OF CONSTITUENT PARTICLES IN CRYSTALS

In order to understand the packing of atoms, ions or molecules in the crystals, we consider them as packings of identical solid spheres. There can be many possible arrangements in packing of spheres. Considering the attraction between the spheres, they will prefer close packing in order to get an energetically stable arrangement. The packing can be considered in terms of the stacking or placing of closely packed layer one upon the other. Out of the two arrangements, (*a*) and (*b*), shown in Fig. 3.8. the arrangement (*a*) is more closely packed than that in (*b*). Further, it may be seen that in the more closely packed arrangement, any one sphere is in contact with six others which make a hexagon pattern around, *i.e.*, it has six nearest neighbours (Fig. 3.9). The number of nearest neighbours is called its *coordination number*.

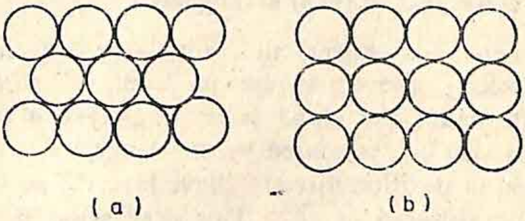


Fig. 3.8 Close packing of spheres in two dimensions.

Now, how we shall see the successive layers are arranged on the first layer '*a*'(shown by solid circles in Fig.3.10. In the second layer, '*b*' (shown bv broken circles, Fig. 3.10), each sphere is situated at the depression created at the centre of the three touching spheres of the first layer. Each sphere in the first layer has six depressions surrounding it. Out of these, three alternate positions are marked as *A* and the remaining three are marked as *B*. In the second layer, the spheres are situated in such a way that they take the positions marked as *A* while the depressions *B* remain unoccupied (Fig. 3.10). Each sphere thus touches nine other spheres. The depressions *B* are unoccupied because the holes *A* and *B* cannot be occupied at the same time due to shortage of space between the two adjacent holes. So, either all *A* or all *B* holes can be occupied at one time by the second layer.

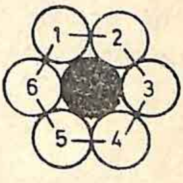


Fig. 3.9. Any sphere is in contact with six others.

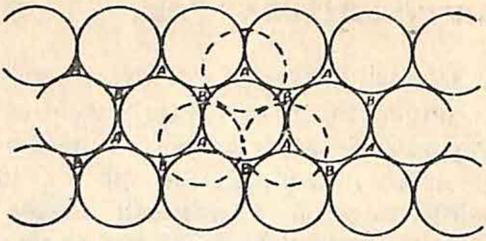


Fig. 3.10. Second layer (broken circles) occupying the alternate hollow positions (*A*) of the first layer.

The third layer can be packed on the top of the second layer, *b*, in two ways:

Hexagonal close packed (hcp) arrangement

In the *hcp arrangement*, the third layer is placed so that each sphere is directly above a sphere in layer '*a*' (Fig. 3.11). This arrangement makes the third layer like layer '*a*' in every respect and so it can also be designated by the letter '*a*'. A fourth layer can be placed in position directly above layer '*b*' so that the former can also be designated as '*b*'. This alternating pattern of '*a*' and '*b*' layers can be extended upwards to the desired extent and designated as *ab*, *ab*, *ab*, ... pattern. In this pattern, each sphere touches 12 others (coordination number is 12) and is called hexagonal close packing (hcp).

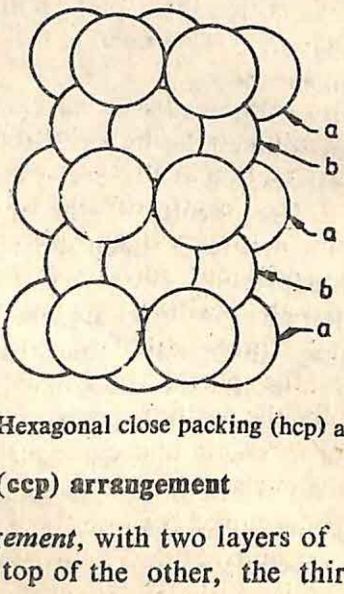


Fig. 3.11. Hexagonal close packing (hcp) arrangement.

Cubic close packed (ccp) arrangement

In the *ccp arrangement*, with two layers of spheres '*a*' and '*b*' arranged one on the top of the other, the third layer '*c*' can be placed on the layer '*b*' so that the spheres of the layer '*c*' are not directly above the spheres in layer '*a*' (Fig. 3.12). In this case, the layer '*c*' is different from either of the two layers '*a*' and '*b*'. The spheres of this layer are placed over the depressions *B* of the first layer. The fourth layer can be directly placed above the layer '*a*' and the fifth above the layer '*b*' so that the pattern of the arrangement can be designated as *abc*, *abc*, *abc*,. .. .In this pattern also each sphere is in contact with 12 spheres (coordination number is 12) and is called cubic close packing (ccp).

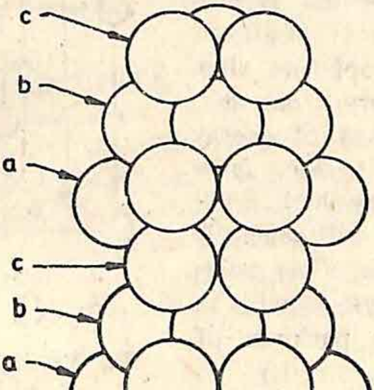


Fig. 3.12. Cubic close packing (ccp) arrangement.

Most of the metals possess either hcp or ccp arrangement. For example, Be, Mg and Mo crystallize in the hcp structure while Al, Fe, Ni, Cu, Ag and Au crystallize in the ccp structure. In these arrangements, 26% of the space is unoccupied and may be regarded as *holes* or *voids* in the crystal lattice. Two different types of holes occur. Those bonded by four spheres are called *tetrahedral holes* or *voids* (Fig. 3.13, a) and those bonded by six spheres are called *octahedral holes* or *voids* (Fig. 3.13, b). For every sphere in

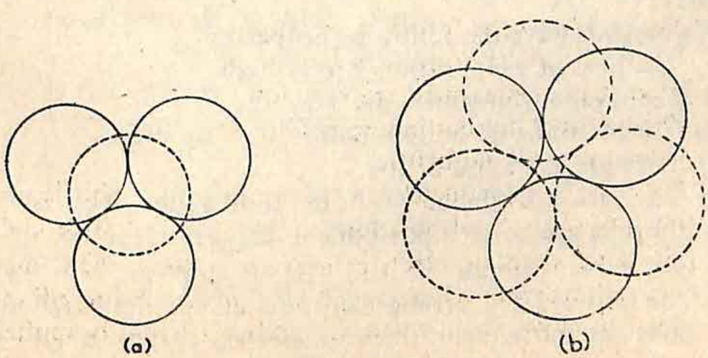


Fig. 3.13. Holes or voids in crystals.

the arrangement, there will be one octahedral hole and two tetrahedral holes. The octahedral holes are larger than the tetrahedral holes.

3.6. IONIC CRYSTALS

These crystals are made up of positive (cations) and negative (anions) ions so that the crystal as a whole is electrically neutral. In sodium chloride, for example, the units are Na^+ and Cl^- ions. Each ion of a given sign is held by electrostatic forces of attraction to all ions of opposite sign. These forces are very strong and, therefore, the amount of energy required to separate ions from one another is very high. The cations and anions will generally be of different sizes. The voids or holes in such crystals will be wider than those in packings of equal spheres (as in metals). In ionic crystals, there are two interpenetrating lattices of anions and cations. In NaCl, it has been found that distance between two adjacent ions is 2.81Å. On adding the ionic radii of sodium (0.95Å) and chlorine (1.81Å), we find that there is a little space between ions. Structure of solid NaCl (Fig. 3.14) is a special case of ionic crystals. Here the coordination number of each ion is 6. It may be kept in mind that every ion in the unit cell interacts with every other ion so that the whole crystal can be considered as a single *giant molecule*. Halides of lithium, sodium, potassium, rubidium, silver, and oxides and sulphides of magnesium, calcium, strontium, barium, manganese and nickel possess sodium chloride structure.

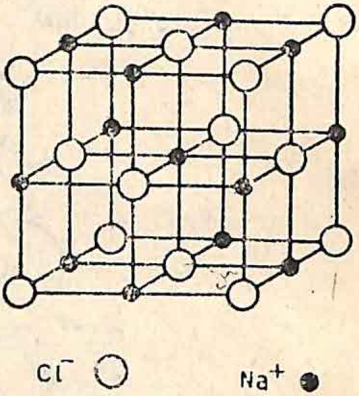


Fig. 3.14. Ionic crystal structure of NaCl.

Ionic crystals have the following properties:

(i) The heat of evaporation is very high.
(ii) Their vapour pressures are very low.
(iii) The melting and boiling points are very high.
(iv) They are hard and brittle.
(v) They are bad conductors in the solid state. This is because the ions are in fixed positions in the crystal lattice and cannot move when an electric field is applied. On melting, the well-ordered arrangement of ions is destoryed and the ions can move about when an electric current is applied.

(vi) Ionic solids behave as good conductors (electrolytes) in aqueous solution. This is because water breaks the electrostatic forces between ions and make them mobile because of its high dielectric constant.

(vii) Unlike metallic crystals, ionic crystals have different particles in their neighbourhood. This difference checks an easy slip between neighbouring ions in an ionic crystal. Thus ionic crystals may break under stress while metals show ductility and malleability.

(viii) Ionic crystals are soluble in water but insoluble or slightly soluble in organic solvents such as benzene, ether, etc.

3.7. DEFECTS IN CRYSTALS

If in a crystal, the constituent particles are arranged in a regular fashion, the structure is called an *ideal structure*. However, no crystal structure is perfect, i.e., every ionic structure shows some imperfections or deviations which are called *defects*. The deviations arise because some ions do not occupy the theoretical positions. The defects in different types of ionic solids are briefly described below.

Defects in Stoichiometric Solids

Stoichiometric solids are those in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae. In these compounds two types of defects are observed. These are known as *Schottky defects* and *Frenkel defects*.

SCHOTTKY DEFECTS

A pair of 'holes' exists in the crystal lattice due to one cation and one anion missing from the crystal lattice (Fig. 3.15). The crystal as a whole remains neutral because the number of missing cations and anions remains the same. This sort of defect occurs in highly ionic compounds with a high coordination number and where the ions (both cations and anions) are of similar size. Alkali halides such as NaCl and CsCl show this defect.

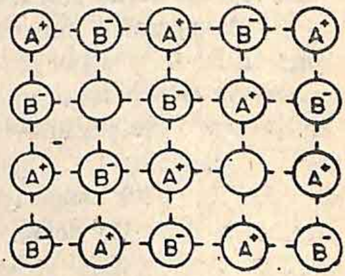


Fig. 3.15. Schottky defects.

FRENKEL DEFECTS

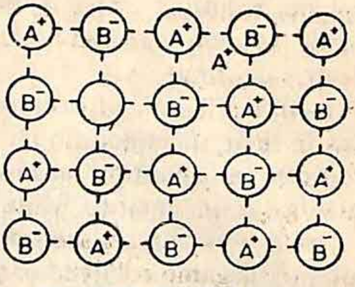


Fig. 3.16. Frenkel defects.

When a 'hole' exists in the crystal lattice because an ion occupies interstitial lattice site, it gives rise to Frenkel defect (Fig. 3.16) The defect occurs more frequently in solids which have low coordination number and possess ions (cations and anions) of different sizes. Since cations are generally smaller than anions, it is more common to find the cations occupying the interstitial sites. For example, in AgBr and ZnS crystals, Ag^+ ions and Zn^{2+} ions are missing from the lattice sites and are present in the interstitial positions.

As a result of Schottky and Frenkel defects in crystalline solids, their electrical conductivity, lattice energy and density decrease. The solids acquire some covalent character.

Defects in Non-stoichiometric Solids

Non-stoichiometric solids are those in which the ratio of positive and negative ions present differs from that indicated by the ideal chemical formula. In compounds such as FeO, FeS, CuO, TiO, ZrO and Cu_2S, the real composition of the constituent ions can vary. Cuprous sulphide, for example, may contain anything between $Cu_{1.96}S$ and Cu_2S. The balance of positive and negative charges is maintained either by having extra electrons or extra positive charges present. This makes the structure irregular, *i.e.*, it contains the defect in addition to Schottky and Frenkel defects. These additional defects arise because either the metal or non-metal atoms are present in excess.

METAL EXCESS DEFECT

This occurs because of the following:

(i) A negative ion may be missing from its lattice site, leaving a hole which is occupied by an electron thereby maintaining the electrical neutrality (Fig. 3.17). This defect is rather similar to Schottky defect and is found in crystals which are known to have Schottky defects. For example, when NaCl is treated with sodium vapours, a yellow

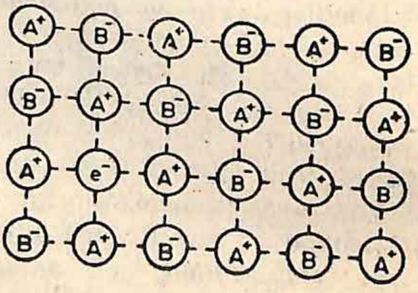


Fig. 3.17. Metal excess defect due to missing anion.

coloured non-stoichiometric form NaCl is obtained in which there is an excess of sodium ion.

(ii) A second way in which metal excess defect occurs, when an extra positive ion occupies an interstitial position in the lattice. An electron which is also present in an interstitial position helps to maintain the electrical neutrality. This is illustrated in Fig. 3.18. This defect is like Frenkel defect and is much more common than the first. It is found in crystals which are expected to have Frenkel defects.

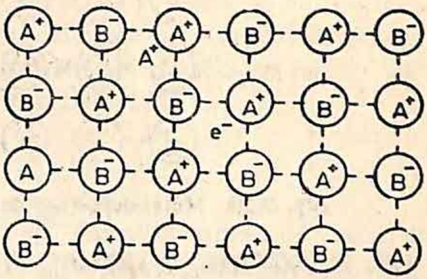


Fig. 3.18. Metal excess defect caused by interstitial cation.

Crystals with either type of metal excess defects contain free electrons and if these migrate, they conduct electricity. Since there are few defects (hence a few free electrons), the amount of current carried is very small. These crystals thus act as *semi-conductors.*

The free electrons in such crystals can be excited to higher energy levels giving absorption spectra and as a consequence the compounds get coloured. ZnO is yellow when hot and white when cold.

METAL DEFICIENCY DEFECT

This defect occurs in metals with variable oxidation states, *i.e.*, the transition metals. It can take place in either of the following two ways:

(i) A cation may be missing from its lattice site but the electrical neutrality is maintained when the adjacent metal ion acquires higher oxidation state (Fig. 3.19). FeO, FeS and NiO provide examples of this type of defect.

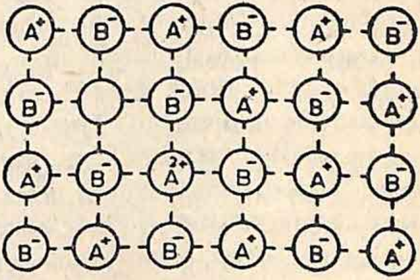


Fig. 3.19. Metal deficiency defect caused by missing cation.

(ii) An extra negative ion may be present in an interstitial site. The corresponding increase in the negative charge is balanced by the oxidation of an adjacent metal ion (Fig. 3.20). Since anions are usually large, it is difficult to expect them to be present at interstitial sites. Crystals with metal deficiency defects act as semi-conductors.

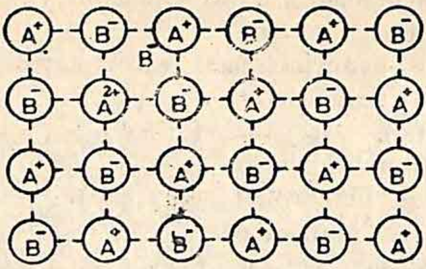


Fig. 3.20 Metal deficiency defects caused by interstitial anion.

3.8. ELECTRICAL CONDUCTANCE IN SOLIDS

Based on the electrical conductance, solids may be divided into three types: (i) Metals, (ii) Insulators and (iii) Semi-conductors. Conductance in solids varies from 10^8 ohm^{-1} cm^{-1} in metals to 10^{-22} ohm^{-1} cm^{-1} in insulators. This is one of the characteristic properties of the solids and indicates their internal structures and the types of bonding.

In *metals*, conductance is due to the movement of mobile electrons in the metal crystal (recall electron 'sea' model which you have studied in class XI).

Most of the organic and inorganic compounds are *insulators* or bad conductors. However, ionic solids may conduct electricity to a very small extent though they are classified as insulators. The presence of interstitials causes conduction in the ionic solids as studied in the previous section.

Semi-conductors have their conductance values between those of metals and insulators and lie in the range 10^2 to 10^{-9} ohm^{-1} cm^{-1}. Silicon and germanium are the most common examples of semiconductors. Atoms of both these elements have four electrons in the outermost shell. Each atom is covalently bonded with four neighbouring atoms giving rise to a highly stable tetrahedral structure as in diamond. There are no free electrons and hence the conductance is very low. On providing enough energy (say heat), some of the covalent bonds break and electrons get removed from their normal positions. These electrons then migrate leaving behind a positive charge (positive hole) at the site of the missing bond. Now, on applying the electric field, the electrons migrate in one direction and the positive holes in the other. The solid thus acquires some conductance and it is known as ***intrinsic conductance*** (because it is produced in the solid without adding any external substance). On adding some impurity, for example arsenic, the conductance increases, Out of five the valence shell electrons in arsenic, four form covalent bonds with the surrounding atoms and the fifth remains free which can carry current easily. This is called *extrinsic conductance*.

Conductance of metals decreases with temperature while that of semi-conductors increases with temperature. Semi-conductors find applications in the manufacture of transistors.

3.9. ALLOYS

Alloys are solid solutions produced from mixtures of two or more metals or from metals and non-metallic elements such as carbon and nitrogen. Their properties are distinctly different from those of the constituent elements. This is because the alloys often show crystal defects which are responsible for the special characteristics imparted to the alloys. Alloying of iron with carbon and several other elements such as chromium, manganese, nickel and tungsten, induces hardness and makes the resulting alloy rust-resistant. Pure gold is soft, but when alloyed with copper or silver, it can be easily handled. Alloys are also produced to: (i) increase tenacity (as in *brass*, an alloy of copper), (ii) get better castings (as in *type metal*, an alloy of lead), (iii) improve colour (*aluminium bronze*, an alloy of aluminium) looks like gold, (iv) lower melting points (like *solder* alloy), and (v) modify chemical properties (as in *amalgams* alloys in which mercury is one of the constituents).

3.10. LIQUID CRYSTALS

As the name suggests, *liquid crystals* are the states of matter intermediate between the liquid and the crystalline states. Some of their properties are similar to those of liquids and some to those of crystals. The crystalline state is a regular three-dimensional arrangement of the constituent particles and this justifies its regular external shape. The liquid state does not possess long range order of molecules and hence it flows and assumes the shape of the container.

We all know that when a crystal melts, it is changed to the liquid state. However, if the crystal consists of long rod-like molecules (Fig. 3.21, a) it may exhibit two or sometimes more melting points before it finally goes to the ordinary isotropic (same in all directions) liquid state (Fig. 3.21, c). In these intermediate states, the material is viscous, turbid (if in bulk) and appears to be quite distinct from the normal liquid. These states are known as *liquid* *crystalline states* or *mesophases* (Fig. 3.21, b)

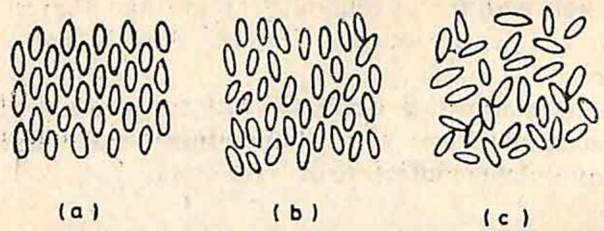


Fig. 3.21 Arrangement of rod-like molecules in (a) crystal, (b) liquid crystal and (c) isotropic liquid.

Several thousand compounds are known which behave as liquid crystals. Two examples are given below:

p-Azoxyanisole

solid crystal $\overset{389K}{\rightleftharpoons}$ Liquid crystal $\overset{408K}{\rightleftharpoons}$ Isotropic liquid *n-p-Methoxy benzolidene-p-butylaniline* (abbreviated as *MBBA*) Solid crystal $\overset{295K}{\rightleftharpoons}$ Liquid crystal $\overset{320K}{\rightleftharpoons}$ Isotropic liquid

Because of their electrical and optical properties, liquid crystals find immense use in watches, calculators and many other instruments as liquid crystal displays, LCD (Fig. 3. 22). They consume the least electrical power of all known types of display systems.

Fig. 3.22 Liquid crystal display.

EXERCISES

3.1 How are solid classified?

3.2 Give the distinguishing features of amorphous and crystalline solids.

3.3 Give the types of crystals according to the units, types of binding forces and their properties.

3.4 How will you show that a particular substance is a crystalline substance?

3.5 Discuss the study of the structures of crystals by X-rays.

3.6 What is Bragg's equation? Give the significance of terms used in the equation.

3.7 Define the following:
  - (i) Crystal lattice.
  - (ii) Unit cell.
  - (iii) Coordination number.

3.8 Name the different crystal systems with appropriate examples. Give the axial distances and the axial angles of the systems.

3.9 Explain the packing of constituent particles in crystals.

3.10 What are 'hcp' and 'ccp' arrangements in crystals?

3.11 Draw diagrams of 'hcp' and 'ccp' arrangements in metals. Give the examples of metals which are found in these packings.

3.12 What are tetrahedral and octahedral voids? Explain with the help of appropriate diagrams.

3.13 What are ionic crystals? Discuss their characteristics.

3.14 Draw the unit cell of NaCl and explain its features.

3.15 What do you understand by crystal defects?

3.16 What are the defects observed in stoichiometric crystals and what changes do they induce in the crystals?

3.17 (i) What are non-stoichiometric crystals?
(ii) What are the common defects observed in them?
(iii) Explain the consequences of metal excess defect.

3.18 Determine the distance between two parallel planes when X-rays of wavelength 0.16 nm give a first order diffraction from the surface of a crystal. The angle of diffraction, $\theta = 8°$. **(Ans. 0.576 nm)**

3.19 Write short notes on the following:
(i) Insulators.
(ii) Semi-conductors.
(iii) Alloys.
(iv) Liquid crystals.

Unit 4

More about Chemical Energetics

Quantitative aspects of conservation of energy. Driving force of reactions (free energy change), concepts of entropy (order-disorder). Examples to illustrate concepts of free energy and entropy (simple treatment of these topics).

In class XI, we have learnt about internal energy, E, enthalpy, H, Hess's law, etc. Now, we shall try to have more understanding of energy changes which occur during the course of chemical reactions.

4.1. CONSERVATION OF ENERGY

We are familiar with the fact that the total energy in the universe is present either as kinetic energy or as potential energy. During a physical or chemical change, (*i*) the energy may change from kinetic to potential and *vice versa*, (*ii*) the energy may be transferred from one portion of the matter to another. In the latter case, the energy is transferred in any of the following ways: (*i*) Heat, (*ii*) Work or mechanical energy, (*iii*) Electrical energy and (*iv*) Light or radiation, etc.

The law of conservation of energy states that '*in the universe, energy can neither be created nor destroyed, although it may be converted from one form to the other.*' Thus, whenever energy in one form disappears, an equal amount of energy in some other form must appear.

When some energy in the form of heat is absorbed by the system, a part may be used to change (increase) the internal energy of the system while another part may be used in doing work. This work could be mechanical work of expansion, electrical work, etc. Since energy is conserved,

Heat absorbed = Increase in internal energy of the system + Work done by the system on the surroundings.

Work done by the system = Expansion work + Non-expansion work

The non-expansion work is also directed into useful effects and is called *useful work*. We can write the above information in the form of symbols as :

$$Q=\Delta E+W_{\text{expansion}}+W_{\text{non-expansion}}$$
$$=\Delta E+W \qquad (4.1)$$

where Q is the heat absorbed by the system, ΔE is the increase in its internal energy and W is the work done by the system on the surroundings.

If the system is under a constant pressure, P, and its volume increases by a small value ΔV, the work done, $W=P\times\Delta V$. The equation (4.1) takes the form :

$$Q=\Delta E+P\Delta V \qquad (4.2)$$

When we burn petrol in the engine of a scooter, a part of the heat raises the temperature of the engine (increase in internal energy) while the other part imparts the desired mechanical motion to the scooter.

4.2. INTERNAL ENERGY, *E*

The internal energy, E of a substance is the sum of different forms of energy like (*i*) energy of translation of molecules, (*ii*) energy of rotation of molecules, (*iii*) energy of vibration of molecules, (*iv*) coulombic energy of electrons and nuclei in atoms, and (*v*) interaction energy of constituent particles in the substance. A system in a particular state has the same internal energy, irrespective of the manner by which it is made.

Molecules of monoatomic gases have only translation (kinetic) energy since rotations and vibrations are only possible in diatomic and polyatomic molecules. Our previous knowledge tells us that kinetic energy of the one mole of such a gas is equal to $(3/2)RT$. Thus,

$$E_k=\tfrac{3}{2}RT \qquad (4.3)$$

4.3. ENTHALPY, *H*

The heat content of a substance is called enthalpy, H, and is given by:

$$H=E+PV \qquad (4.4)$$

The change in enthalpy, ΔH, is the difference between the enthalpy of the products (H_{products}) and that of the reactants ($H_{\text{reactants}}$). Thus,

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

For a process taking place at a constant pressure, we can write equation (4.2) as:

$$Q = \Delta(E + PV)$$
$$= \Delta H \text{ (from equation 4.4)}$$

Thus $\quad \Delta H = Q = \Delta E + P\Delta V \qquad (4.5)$

It means the change in enthalpy (ΔH) equals the heat absorbed by the substance and is equal to the change in internal energy plus any pressure volume work done.

As the monoatomic gases possess only the kinetic energy, the enthalpy H, per mole of such a gas at a temperature, T, is given by:

$$H = \tfrac{3}{2} RT + PV \text{ (from equations 4.3 and 4.4)}$$

Since $\quad PV = RT$

Therefore $\quad H = \tfrac{3}{2} RT + RT = \tfrac{5}{2} RT \qquad (4.6)$

Putting the values of R and T, in the above equation, the value of H can be obtained.

4.4. SPONTANEOUS CHEMICAL CHANGE

When a system under given conditions undergoes a direct physical or chemical change without the assistance of an external agency, the process is called a *spontaneous process*. On the other hand, a process which has no natural urge to occur is said to be a *non-spontaneous process*. Some of the familiar examples of spontaneous processes are:

(i) Vaporization of water in an evacuated vessel.

$$H_2O\ (l) \rightarrow H_2O\ (g)$$

(ii) Reaction between hydrogen gas and iodine vapour to form hydrogen iodide.

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

(iii) Dissolution of sugar in water to form a solution.

Besides, some processes require some initiation to proceed. For example,

(i) Hydrogen gas reacts with oxygen to produce water only when the reactants are ignited.

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightarrow H_2O\ (l)$$

(ii) Methane burns in oxygen when ignited to give carbon dioxide and water.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

4.5. CAUSES OF SPONTANEITY

Over a century back, in 1878, Thomson and Berthelot suggested the *decrease in energy* as measured by the heat evolved (ΔH) in an exothermic reaction was the cause of spontaneity of a reaction. In support, they cited many examples like,

(i) $C + O_2 \rightarrow CO_2$; $\Delta H = -394$ kJ

(ii) $N_2 + 3H_2 \rightarrow 2NH_3$; $\Delta H = -94$ kJ

In these examples, the products have a lower energy than the reactants. However, this suggestion does not appear to be correct because:

(a) Many endothermic reactions like dissolution of KNO_3 or NH_4Cl in water, evaporation of water, etc., are also spontaneous.

(b) Spontaneous reactions do not go to completion even though ΔH remains negative throughout.

(c) Reversible reactions also take place. Some examples are:

(i) $H_2 + I_2 \rightleftharpoons 2HI$

(ii) $CH_3COOH + C_2H_5OH \rightleftharpoons H_2O + CH_3COOC_2H_5$
Acetic acid Ethyl alcohol Ethyl acetate

Thus it is clear that decrease in energy or negative sign of ΔH is not the sufficient criterion for determining the spontaneity of a process.

Let us now take up another explanation for spontaneity. Consider a spontaneous process where there is no energy change, i.e., $\Delta H = 0$. The diffusion of two gases into each other is one such process. The diffusion begins as soon as the contact between them is made. In Fig. 4.1 (a), the left-hand compartment contains gas I (shown by ●) whilst the right-hand compartment contains gas II (shown by o). The two gases are separated by a movable partition. When the partition is removed (Fig. 4.1 b), the gases diffuse into each other and thorough mixing takes place. We can say that after diffusion a state of maximum *randomness*, *chaos* or *disorder* results. The expansion of a gas into vacuum is a related

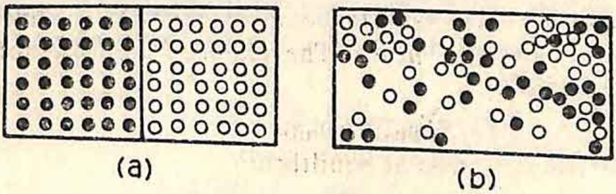


Fig. 4.1. Increase in randomness on diffusion of gases.

example of spontaneity. It is accompanied by an increase in the degree of disorder of the system.

In endothermic reactions (where ΔH is positive), there can also be an increase in randomness. Let us consider some examples :

(i) Decomposition of mercuric oxide.

$$2HgO(s) \longrightarrow 2Hg(l)+O_2(g)$$

The process takes place in the direction of greater randomness. Here the gaseous state is more random than liquid state which in turn is more random than the solid state.

(ii) Dissolution of NaCl in water.

$$NaCl(s)+aq \longrightarrow Na^+(aq)+Cl^-(aq)$$

The ions held together in the solid crystal lattice become free and move about in all directions. It means the order has given place to disorder.

(iii) Water changes into vapour.

$$H_2O(l) \longrightarrow HO(g)$$

The gaseous phase is more random than liquid phase. In other words, the process proceeds in the direction of increased randomness.

(iv) Dissociation of HI.

$$2HI(g) \longrightarrow H_2(g)+I_2(g)$$

The identical HI molecules dissociate to hydrogen and iodine molecules. The mixing of two different kinds of gaseous molecules creates a more random situation than that obtained by identical type of molecules.

From the above examples, it is clear that the processes where ΔH is zero or positive can also be spontaneous provided there is tendency for maximum disorder or randomness. Thus the tendency of a process to go to a state of *maximum randomness* is an important factor that determines its spontaneity.

4.6. ENTROPY, S

This property of a substance called entropy, S, measures randomness or disorder in it. The change in entropy of a system is represented by ΔS.

$$\Delta S=S_{\text{final}}-S_{\text{initial}}$$

In a reversible reaction at equilibrium,

$$\Delta S=\frac{Q}{T}=\frac{\Delta E+P\Delta V}{T} \qquad (4.7)$$

The heat gained $(+Q)$ in the forward reversible process is equal to heat lost $(-Q)$ in the backward reversible process Thus

$$\Delta S = \frac{Q}{T} + \left(\frac{-Q}{T}\right) = 0 \tag{4.8}$$

For an irreversible or spontaneous process,

$$\Delta S > \frac{Q}{T}$$

or $$\Delta S > \frac{\Delta E + P\Delta V}{T}$$

or $$\Delta S > 0 \tag{4.9}$$

Thus in naturally occurring processes, the system tends to change in such a manner that the entropy of the system increases. We may conclude that the *spontaneity of a process takes place in the direction of increasing entropy.*

Let us consider the process of fusion and that of vaporization to explain the relationship between randomness and entropy.

4.7. ENTROPY OF FUSION

When ice melts,

$$\text{Ice (s)} \rightleftharpoons \text{Water (l)}$$

$$S_l - S_s = S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_f} \tag{4.10}$$

where S_l is the entropy per mole of liquid water, S_s the entropy of solid ice, ΔH_{fus} the enthalpy of fusion and T_f the fusion temperature of ice. Since ΔH_{fus} for meting of ice$=6025$ J mol^{-1}, $T_f = 273$ K,

$$\Delta S_{\text{fus}} = \frac{6025 \text{ J mol}^{-1}}{273 \text{ K}} = 22.1 \text{ J k}^{-1} \text{ mol}^{-1}$$

Since ΔH_{fus} is positive, ΔS_{fus} is also positive and $S_l > S_s$ or the liquid state is a state of greater disorder. Thus we infer that entropy is a measure of the randomness or disorder.

4.8. ENTROPY OF VAPORIZATION

$$\Delta S_{\text{vap}} = S_g - S_l = \frac{\Delta H_{\text{vap}}}{T_b} \tag{4.11}$$

where ΔH_{vap} is the enthalpy of vaporization per mole and T_b the boiling point. For ethyl alcohol, $\Delta H_{\text{vap}} = 38.58$ kJ mol^{-1} and $T_b = 351.5$ K. Hence,

$$\Delta S_{\text{vap}} = \frac{38.58 \text{ kJ mol}^{-1}}{351.5 \text{ K}} = 0.1098 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$= 109.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

Here also ΔS_{vap} is positive or $S_g > S_l$. (4.12)

It is known that gaseous state has a greater randomness than liquid state (where some degree of order exists). Hence again, entropy can be taken as a measure of disorder, randomness or chaos in a system.

Example 4.1. Calculate the entropy change associated with the vaporization of 1 mol of $C_2H_5OC_2H_5$. The heat of vaporization of ether is 27.2 kJ mol^{-1} and its boiling point is 308 K.

Solution

$$\Delta S_{\text{vap}} = \frac{27.2 \text{ kJ mol}^{-1}}{308 \text{ K}} = 0.0883 \text{ kJ K}^{-1} \text{ mol}^{-1} = 88.3 \text{ J K}^{-1} \text{ mol}^{-1}.$$

4.9. FREE ENERGY

We introduce a new function called *free energy* to understand the true criterion for spontaneity of a process. It is denoted by the symbol G, known as Gibbs free energy. It is related to E, H, S and T by the following equations:

$$\begin{aligned} G &= H - TS \\ &= E + PV - TS \quad \text{(since } H = E + PV\text{, equation 4.4)} \end{aligned} \qquad (4.13)$$

$$\begin{aligned} \text{Also, } \Delta G &= \Delta H - \Delta(TS) \\ &= \Delta E + \Delta(PV) - \Delta(TS) \end{aligned} \qquad (4.14)$$

For a change at constant temperature and constant pressure, the term $\Delta(PV)$ can be replaced by $P\Delta V$ and the term $\Delta(TS)$ by $T\Delta S$, we then write

$$\begin{aligned} (\Delta G)_{T,P} &= \Delta E + P\Delta V - T\Delta S \\ &= \Delta H - T\Delta S \text{ (since } \Delta E + P\Delta V = \Delta H\text{, equation 4.5)} \end{aligned} \qquad (4.15)$$

In equation (4.15), the term ΔG can be split into two quantities:

(i) ΔH. A negative value of ΔH, corresponding to an exothermic reaction, leads to a negative value of ΔG. This confirms the common observation that exothermic reactions, at ordinary temperature and pressure, tend to be spontaneous.

(ii) $T\Delta S$. A positive value of ΔS tends to make ΔG negative and the process will be spontaneous.

Thus, we infer, if ΔG is negative (or <0), the process will be spontaneous.

ΔG can be negative not only when ΔH is negative and ΔS is positive but also when ΔH is positive (as in the case of dissolution of NH_4Cl) provided the factor $T\Delta S > \Delta H$ and is positive. When ΔH is negative (favourable), and $T\Delta S$ is also negative (unfavourable), the ΔG can be negative if the numerical value of ΔH exceeds the value of $T\Delta S$.

Thus, it can be concluded that the sign of ΔG gives the real idea about the spontaneity of a reaction. This can be summarized by saying that:

(1) The process is spontaneous when ΔG is negative (or <0).

(ii) The system is in equilibrium or there is no net reaction in any direction when $\Delta G=0$.

(iii) The reaction does not occur or proceeds only in the reverse direction when ΔG is positive.

4.10. PHYSICAL SIGNIFICANCE OF FREE ENERGY

From equation (4.1), we know

$$Q=\Delta E+W_{\text{expansion}}+W_{\text{non-expansion}}$$

At constant pressure, $W_{\text{expansion}}=P\Delta V$

$$\text{Therefore, } Q=\Delta E+P\Delta V+W_{\text{non-expansion}}$$

$$=\Delta H+W_{\text{non-expansion}} \qquad (4.16)$$

(since $\Delta E+P\Delta V=\Delta H$, equation 4.5)

From equation (4.7), we know that in a reversible reaction at constant T,

$$\Delta S=\frac{Q}{T}$$

$$\text{or} \qquad Q=T\Delta S \qquad (4.17)$$

Substituting the value of Q from equation (4.17) into equation (4.16), we get:

$$T\Delta S=\Delta H+W_{\text{non-expansion}}$$

$$\text{or} \qquad \Delta H-T\Delta S=-W_{\text{non-expansion}} \qquad (4.18)$$

At constant T and P, we know from equation (4.15) that

$$(\Delta G)_{T,P}=\Delta H-T\Delta S$$

Equation (4.18) can thus be written as

$$(\Delta G)_{T,P}=-W_{\text{non-expansion}} \qquad (4.19)$$

Rearranging equation (4.19), we obtain

$$W_{\text{non-expansion}}=-(\Delta G)_{T,P} \qquad (4.20)$$

For most purposes, non-expansion work can be converted into useful work. It is evident from equation (4.20) that the decrease in free energy during any change $(-\Delta G)$ is a measure of the useful or net work done during the change. We can, therefore, say that free energy, G, of a system is a measure of its capacity of doing useful work. It is only a part of the energy of the system which is available for conversion into useful work and hence is called *free energy*.

If in a system, the increase in free energy and enthalpy be ΔG and ΔH respectively, the *efficiency* of the process is given by

$$\text{Efficiency}=\frac{\Delta G}{\Delta H}=\frac{\text{Useful work obtained from the system}}{\text{Total energy absorbed by the system}}$$

The effeciencies of some power devices such as heat engine, electricity to light, dry cell and fuel cell are 30%, 40%, 70% and 100%, respectively.

4.11. CONDITIONS FOR EQUILIBRIUM AND SPONTANEOUS CHANGES

For a system to be in equilibrium, the conditions are:

$$(dS)_{E,V}=0$$

and $$(dG)_{T,P}=0$$

For spontaneous changes, the requirements are:

$$dS>0$$

and $$dG<0$$

4.12. RELATION BETWEEN PROBABILITY OF A PROCESS AND TEMPERATURE

Whether a process can occur at a particular temperature or not can be predicted by using equation (4.15),

$$(\Delta G)_{T,P}=\Delta H-T\Delta S$$

Let us illustrate this point by taking the case of vaporization of water at 1 atm.

$$H_2O(l) \longrightarrow H_2O(g)$$

For this process, $\Delta H=40.63$ kJ mol^{-1} and $\Delta S=108.8$ J K^{-1} mol^{-1}

Hence, $\Delta G=40.63\times10^3$ J mol^{-1}$-T\times108.8$ J K^{-1} mol^{-1}

The equilibrium will be reached at boiling point at 1 atm. At this temperature, the change will occur reversibly and ΔG becomes zero. The temperature at which $\Delta G=0$ is given by:

$$T=\frac{40.63\times10^3}{108.8}=373.4\text{ K}$$

This result is very close to the boiling point of water at 1 atm pressure. When $T>373.4$ K, $\Delta G<0$, the vaporization will become spontaneous and continuous.

4.13. PREDICTION FOR THE SIGN OF ΔH

It is possible to determine the sign of ΔH by adopting the following guidelines:

(i) Reactions in which more bonds are broken than formed are endothermic (*i.e.*, positive ΔH). Thus

$$\underset{\text{Ethanol}}{CH_3CH_2OH(g)} \longrightarrow \underset{\text{Ethylene}}{CH_2{=}CH_2(g)}+H_2O(g)$$

(ii) Reactions in which bond formation occurs are generally exothermic (*i.e.*, negative ΔH). Thus

$$I(g) + I(g) \longrightarrow I_2(g)$$

is an exothermic reaction since I—I bond is formed.

(iii) Reactions in which bonds between unlike atoms are formed starting with homoatomic molecules are also exothermic. For example,

$$H{-}H(g) + Cl{-}Cl(g) \longrightarrow 2H{-}Cl(g)$$

is an exothermic reaction.

4.14. PREDICTION FOR THE SIGN OF ΔS

The difference between the entropies of the products and of the reactants, *i.e.*, ΔS can be predicted to have a positive value in some cases like:

(i) Reactions in which the number of molecules of products is more than the number of molecules of reactants. For example,

$$2O_3(g) \longrightarrow 3O_2(g) \qquad \Delta S = +137\ J\ K^{-1}\ mol^{-1}$$

$$N_2F_4(g) \longrightarrow 2NF_2(g) \qquad \Delta S = +198.3\ J\ K^{-1}\ mol^{-1}$$

$$CH_4(g) + H_2O(g) \longrightarrow 3H_2(g) + CO(g) \qquad \Delta S = +212.8\ J\ K^{-1}\ mol^{-1}$$

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g) \qquad \Delta S = +101\ 3\ J\ K^{-1}\ mol^{-1}$$

(ii) Processes in which the solid melts or sublimes, or a liquid boils or evaporates. This is because of greater randomness in the molten or gaseous state.

$$Br_2(l) \longrightarrow Br_2(g) \qquad \Delta S = +93.1\ J\ K^{-1}\ mol^{-1}$$

(iii) Reactions in which a solid decomposes to give one or more gases amongst the products. Thus, for example,

$$Ag_2O(s) \longrightarrow 2Ag(s) + \tfrac{1}{2}O_2(g) \qquad \Delta S = +66\ J\ K^{-1}\ mol^{-1}.$$

EXERCISES

4.1 Explain the phenomenon of conservation of energy.

4.2 How is quantity of heat absorbed related to increase in internal energy and work?

4.3 What do you understand by the terms internal energy and enthalpy of a substance?

4.4 How are Q, ΔH, ΔE, $P\Delta V$ related to each other?

4.5 Give two possible causes to determine the spontaneity of a process.

4.6 What is a spontaneous process? Give examples.

4.7 What conclusions do you draw regarding the spontaneity of reactions based on their exothermic and endothermic nature?

4.8 Give examples to show that some (i) exothermic reactions are spontaneous and (ii) endothermic processes are spontaneous.

4.9 Define the term entropy. What does is signify?

4.10 'Entropy is a measure of randomness'. Discuss the statement with the help of examples.

4.11 Define free energy. How is ΔG related to ΔH and ΔS?

4.12 What will you infer regarding the spontaneity of a process from its ΔG value?

4.13 What is the physical significance of free energy?

4.14 How is the decrease in free energy related to the net work done?

4.15 Calculate the entropy change associated with the vaporization of 1 mol of ethanol. It is given that the heat of vaporization of alcohol is 38.58 kJ mol^{-1} and the liquid boils at 351.5 K. **(Ans. 109.8 J K^{-1} mol^{-1})**

4.16 What are the general guidelines to predict the signs of ΔH and ΔS? Give suitable examples.

Unit 5

Kinetics

Rates of reactions—symbolic expressions and units. Factors influencing rates of reactions (nature of reactants, temperature, concentration, catalyst, radiation)—qualitative treatment only. Activation energy. Rate equation. Molecularity and order of reaction. Specific reaction rate. Half-life period. Role of a catalyst with examples to illustrate it. Enzyme catalysis. Reversible reaction.

Chemical kinetics deals with the study of speed, or rate, of chemical reactions. A number of factors govern the speed of a reaction, *i.e.*, whether it will be a fast reaction or a slow reaction. In this Unit we shall consider such related factors which affect the speed of a reaction.

5.1. FAST AND SLOW REACTIONS

Some reactions are so rapid that they take less than a millisecond for completion. Burning of fuel or reactions involving ionic species like mixing of solutions of sodium chloride and silver nitrate with the instant precipitation of silver chloride, are examples of fast reactions. On the other hand, there are reactions like rusting of iron, which are very slow and take months to complete. In between these two extremes, are reactions which occur at conveniently measurable rates. Inorganic reactions like combination of nitric oxide and oxygen [$2NO + O_2 \longrightarrow 2NO_2$], decomposition of hydrogen peroxide [$2H_2O_2 \longrightarrow H_2O + O_2$], and organic reactions like the interaction of acetic acid and ethyl alcohol,

$$CH_3COOH \;+\; C_2H_5OH \longrightarrow CH_3COOC_2H_5 \;+\; H_2O$$

and hydrolysis of sugar,

$$C_{12}H_{22}O_{11}+H_2O \longrightarrow C_6H_{12}O_6+C_6H_{12}O_6$$

are reactions that take place at moderate rate.

5.2. THE REACTION RATE

The rate of a reaction means the speed or velocity with which the reactants are converted into products. It may be defined in terms of the *change in concentration per unit time* for a reactant or product.

For a reaction, A→B, we can write:

$$\text{Rate of reaction} = \text{Time rate of disappearance of A} = -\frac{d[A]}{dt}$$

where [A] is the concentration of A at time t. The negative sign shows that the concentration of A decreases with increasing time. Also,

$$\text{Rate of reaction} = \text{Time rate of formation of B} = +\frac{d[B]}{dt}$$

where the plus sign shows that the concentration of B increases with increasing reaction time.

Thus,

$$\text{Rate of reaction} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt} \qquad (5.1)$$

Now consider the reaction,

$$2A + B \longrightarrow A_2B$$

$$\text{Time rate of disappearance of A} = -\frac{d[A]}{dt} \qquad (5.2)$$

$$\text{Time rate of disappearance of B} = -\frac{d[B]}{dt} \qquad (5.3)$$

$$\text{Time rate of formation of } A_2B = \frac{d[A_2B]}{dt} \qquad (5.4)$$

The rates expressed in equations (5.2), (5.3) and (5.4) are not equal, because A will disappear at twice the rate that B will decrease or that A_2B will form. Therefore, we express the rate of such a reaction by any of the equivalent derivatives:

$$-\frac{d[A]}{dt} = -2\,\frac{d[B]}{dt} = +2\,\frac{d[A_2B]}{dt} \qquad (5.5)$$

This expression shows that the rate can be different for different species.

Thus, for the reaction,

$$2N_2O_5 \longrightarrow 2N_2O_4+O_2$$

we can write:

$$\text{Rate of reaction} = -\frac{d[N_2O_5]}{dt} = \frac{d[N_2O_4]}{dt} = 2\frac{d[O_2]}{dt}$$

It is clear from the above equations that the rate has the **units** of concentration per unit time. If the concentration is expressed in moles per litre and the time in seconds, the rate will be in mol litre^{-1} sec^{-1}. In case of a gas, its concentration can be expressed in terms of its pressure in atmospheres and the rate in atm sec^{-1}.

A typical concentration-time plot for a reaction is shown in Fig. 5.1. It is clear from the plot that the concentrations of the reactants decrease and those of the products increase with time. The slope of each curve is continuously changing with time. It indicates that the rates of the reaction (since rates of reaction are given by the slopes of the curves) are dependent upon the reaction time and also upon concentration.

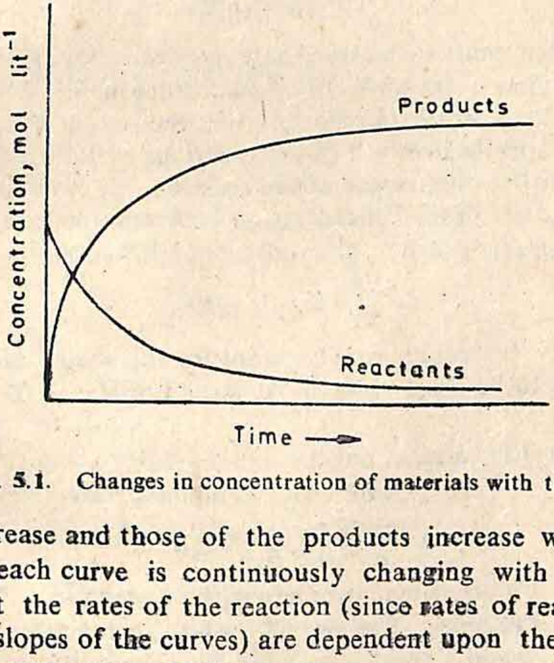


Fig. 5.1. Changes in concentration of materials with time.

5.3. THE RATE LAW

While expressing the reaction rate as a function of the concentration of reactants and products, it is essential to determine experimentally which of the species are actually involved in the rate. The expression which gives the reaction rate as a function of the concentration of each of the substances affecting the rate is known as the *rate equation* or *rate law* for the reaction.

Consider the reaction:

$$2A + B \longrightarrow A_2B$$

If the experimental determination shows that the reaction rate is proportional to the first power of the concentration of A, and is independent of the concentration of B and A_2B, the rate law will be:

$$-\frac{d[A]}{dt}=k\,[A] \tag{5.6}$$

where k is a constant of proportionality. It is known as the *rate constant* or *specific reaction rate* for the reaction. In the above equation, [A] is raised to the first power, the reaction is said to be *first* order in A.

In case the reaction rate is found to depend on the first power of the concentration of A and the square of the concentration of B, the rate law takes the form:

$$-\frac{d[A]}{dt}=k'[A][B]^2 \tag{5.7}$$

where k' represents the specific rate constant for this case. This reaction is *first* order in A and *second* order in B. Also, the reaction will be *overall third* order, *i.e.*, the sum of the orders of the individual species involved in the reaction.

It is possible that in the above reaction, the rate may depend on the third power of the concentration of A and the second power of the concentration of B. The rate law will then be:

$$-\frac{d[A]}{dt}=k''[A]^3[B]^2 \tag{5.8}$$

where k'' is the specific rate constant for this case. Now the reaction is said to be *third* order in A, *second* order in B and *overall fifth* order.

In general for a reaction:

$$aA+bB \longrightarrow \text{Products}$$

$$-\frac{1}{a}\frac{d[A]}{dt}=k\,[A]^m[B]^n \tag{5.9}$$

where m and n are constant numbers for a reaction. These may be integers or fractions. The *overall* order of reaction is given by $(m+n)$ and m and n are determined experimentally. It should be remembered that m may or may not be equal to a, similarly n may or may not be equal to b. Thus the stoichiometry of an equation may not always represent the order of a reaction.

Example 5.1. The following data were obtained at 298K for the reaction

$$S_2O_8^{2-}\,(aq)+2I^-\,(aq) \longrightarrow 2SO_4^{2-}(aq)+I_2\,(aq)$$

Experiment	*Initial conc.* $S_2O_8^{2-}$*, M*	*Initial conc.* I^-*, M*	*Initial rate of increase in conc. of* I_2*, M/min*
I	1.0×10^{-4}	1.0×10^{-2}	0.60×10^{-6}
II	2.0×10^{-4}	1.0×10^{-2}	1.20×10^{-6}
III	2.0×10^{-4}	0.5×10^{-2}	0.60×10^{-6}

What will be the rate equation for the reaction?

Solution. When the data of experiments I and II are compared, it is found that the rate is doubled on doubling the concentration of $S_2O_8^{2-}$ Also, a comparison of the data from experiments II and III reveals that doubling the concentration of I^- means doubling the reaction rate. Thus, the reaction is first order in $S_2O_8^{2-}$ first order in I^-, and overall second order.

$$\text{Rate}=k[S_2O_8^{2-}][I^-]$$

(From the stoichiometry of the equation, one might expect it to be third order reaction.)

5.4. FIRST ORDER REACTIONS

Consider the general first order reaction:

$$A \longrightarrow \text{Products}$$

Let initial concentration of A be a mol litre^{-1} when time $t=0$. Let x moles of A change into products after t seconds. The concentration of A after t second will be $(a-x)$ mol litre^{-1}. We can now write the rate equation after time t as:

$$\frac{dx}{dt}=k(a-x) \tag{5.10}$$

$$\text{or} \quad \frac{dx}{(a-x)}=kdt$$

Integrating, we obtain:

$$-\ln(a-x) = kt + I \tag{5.11}$$

where I is the integration constant. Now, when $t=0$, $x=0$. Substituting this condition in the above equation:

$$-\ln a=I$$

The equation (5.11) can now be written as:

$$-\ln(a-x)=kt-\ln a$$

$$\text{or} \quad \ln\frac{a}{(a-x)}=kt \tag{5.12}$$

$$\text{or} \quad k=\frac{1}{t}\ \ln\frac{a}{a-x} \tag{5.13}$$

Changing to common logarithms, we get:

$$t=\frac{2.303}{k}\ \log\frac{a}{a-x} \tag{5.14}$$

Equations (5.13) and (5.14) express the integrated rate law relating to first order reactions.

In equation (5.13), the term $\ln\frac{a}{a-x}$ is dimensionless pure number because both a and $(a-x)$ are in the same concentration units.

Thus the units for a first order rate constant, k will be sec^{-1}, min^{-1}, etc., depending on how the time t is expressed. However, for the second order reactions $\left(\text{rate equation: } -\frac{d[A]}{dt}=k[A]^2\right)$ and third order reactions $\left(\text{rate equation: } -\frac{d[A]}{dt}=k[A]^3\right)$, the units of k are litre mol^{-1} sec^{-1} and $litre^2$ mol^{-2} sec^{-1} respectively.

Example 5.2. In the reaction, $(COOH)_2 \longrightarrow CO+CO_2+H_2O$, the following results were obtained:

Time (min)	*Volume (in ml) of* $KMnO_4$ *required for titration of oxalic acid*
0	22.0
300	17.0
450	15.0
600	13.4
1200	7.9

Show that the reaction is of the first order and determine the value of the rate constant.

Solution. From the given data, we have:

	$t\,(min)^{-1}$	a	$(a-x)$
(i)	300	22	17
(ii)	450	22	15
(iii)	600	22	13.4
(iv)	1200	22	7.9

Substituting the values in the first order rate equation, we get:

$$\text{(i)} \qquad k=\frac{2.303}{300}\log\frac{22}{17}=0.00086\ min^{-1}$$

$$\text{(ii)} \qquad k=\frac{2.303}{450}\log\frac{22}{15}=0.00086\ min^{-1}$$

$$\text{(iii)} \qquad k=\frac{2.303}{600}\log\frac{22}{13.4}=0.00086\ min^{-1}$$

$$\text{(iv)} \qquad k=\frac{2.303}{1200}\log\frac{22}{7.9}=0.00086\ min^{-1}$$

The values of k obtained are constant and thus the reaction is of first order. The value of the rate constant, $k=0.00086\ min^{-1}$

5.5. HALF-LIFE PERIOD

The time in which half of a reaction is completed, *i.e.*, half the reacting quantity of any of its reactants have reacted, is known as *half-life period* of the reaction. For a first order reaction, we know:

$$t=\frac{2.303}{k}\log\frac{a}{a-x}$$

Now half life period (denoted by $t_{\frac{1}{2}}$) corresponds to time during which the term $(a-x)$ becomes equal to $\frac{a}{2}$. Thus:

$$t_{\frac{1}{2}}=\frac{2.303}{k}\log\frac{a}{a/2}$$

$$=\frac{2.303}{k}\log 2$$

$$=\frac{2.303\times0.301}{k}=\frac{0.693}{k} \qquad (5.15)$$

Example 5.3

For the reaction, $A \longrightarrow B+C$, the following data were obtained:

Time (in sec)	0	900	1800
Concentration of A	50.6	19.7	7.62

Prove that the reaction is of the first order and culculate how long it will take half the original material to decompose.

Solution. From the given data, we have:

	$t\,(sec)^{-1}$	a	$(a-x)$
(i)	900	50.6	19.7
(ii)	1800	50.6	7.62

Substituting the values in the first order rate equation, we obtain:

(i)
$$k=\frac{2.303}{900}\log\frac{50.6}{19.7}=0.00048\ \text{sec}^{-1}$$

(ii)
$$k=\frac{2.303}{1800}\log\frac{50.6}{7.62}=0.00052\ \text{sec}^{-1}$$

The value of k obtained is constant by following the first order rate equation and hence the reaction is of first order.

Now, half life period, $t_{\frac{1}{2}}=\frac{0.693}{k}$

$$=\frac{0.693}{0.0005}=1386\ \text{seconds.}$$

Thus in 1386 seconds half the original material will decompose

5.6. ORDER AND MOLECULARITY OF A REACTION

We have already discussed that the order of a reaction,

$aA + bB \rightarrow$ Products

is obtained from its rate equation; $-\frac{1}{a}\frac{d[A]}{dt}=k\,[A]^m[B]^n$

The sum $(m+n)$ represents the overall order of reaction, and m and n are determined experimentally.

The rate equation is independent of the reaction stoichiometry. The stoichiometric number of molecules of reactants in a reaction is different from its order. The number of species (molecules, atoms or ions) taking part in a single actual step of a reaction is called the *molecularity* of the reaction. For example, a reaction may be *unimolecular*, *bimolecular* or *trimolecular* depending upon whether one, two or three molecules are taking part in a step of the reaction. The information regarding a series of step reactions, proposed to account for an overall reaction, is called *mechanism of the reaction.*

The differences between order and molecularity of a reaction are summarized in Table 5.1.

TABLE 5.1: Differences Between Order and Molecularity of a Reaction

Order	*Molecularity*
It is the sum of exponents of the molar concentrations of the reactants in the rate equation.	It is the number of molecules of the reactants taking part in a single step chemical reaction.
It may or may not have relation with the stoichiometric equation for the reaction.	It is calculated from the reaction mechanism.
It depends on the experimentally determined rate for the overall reaction.	It depends on the rate determining step reaction in the reaction mechanism.
It may be a whole number or fractional.	It must always be a whole number.
It is determined experimentally and cannot be obtained from a balanced chemical equation.	It is obtained from a single balanced chemical equation.

5.7. FACTORS INFLUENCING RATES OF REACTION

The rate of a reaction is affected by several factors, the important among them are:

(i) Nature of reactants.

(ii) Concentration of reactants.

(iii) Temperature.

(iv) Catalyst.

(v) Radiation.

Let us discuss these factors.

Nature of Reactants

Substances differ in activity and hence in speed with which they react with other substances. For example, the active metals displace hydrogen rapidly and vigorously from acids while less active metals act slowly, if at all. Elements like nitrogen react slowly with other elements. On the other hand, halogens combine with most other elements readily. The nature of the reactants is quite important so far as the rates of reactions are concerned. The rates of reactions are different because of the difference in the nature of their reactants. For instance, the reduction of permanganate ion in acid solution by ferrous ion is instantaneous while it is not so by oxalate ion In these reactions, everything is identical except the nature of the reducing agent but still the reaction rates are quite different.

The nature of the reactants is involved because the *activation energy* (minimum energy that reacting molecules must possess individually on per mole basis before they collide and undergo a chemical change) for effective collisions is different for the interacting species. To illustrate the specific dependence of reaction rates on the nature of reactants, it is essential to choose reactions with similar frequencies of collisions. An excellent example is provided by the following two reactions:

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g) \text{ ....Fast}$$

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \text{ ....Slow}$$

Nitric oxide and carbon monoxide molecules are quite alike and they are reacting with oxygen molecules. Their collision frequencies in the two reactions, under similar conditions of temperature and pressure, are expected to be comparable. But the former reaction is fast because of its low activation energy and the latter reaction slow because of its high activation energy (Fig. 5.2).

Concentration of Reactants

It is evident from the rate equation,

$$-\frac{d[A]}{dt}=k[A]^m[B]^n$$

that an increase in [A] or [B] will increase the rate of reaction proportionally. It is a common observation that greater the concentrations of the reactant molecules per litre more will be the number of collisions between molecules per litre per second leading to higher rate of reaction.

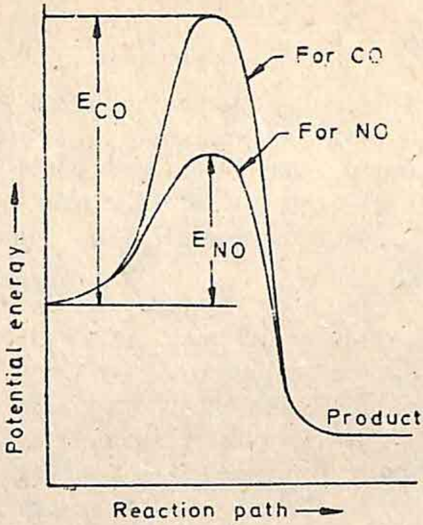


Fig. 5.2. Comparison of energies of CO and NO.

TEMPERATURE

It is found experimentally that an increase in temperature always increases the rate of reaction without changing its order. It is estimated that when the temperature is raised by 10 degrees, the rates of reactions and their rate constants become nearly double.

Arrhenius (1889) found that most reactions obey the equation:

$$\log k = A' - \frac{B}{T} \tag{5.16}$$

where k is the rate constant, T is the absolute temperature, and A' and B are positive constants. A plot of log k against $\frac{1}{T}$ should give a straight line (Fig.5.3) with intercept $= A'$, and slope$=-B$.

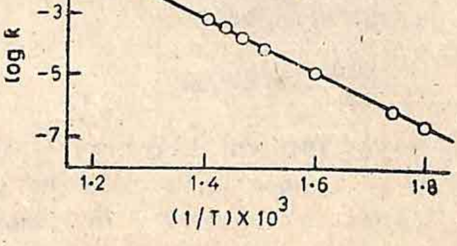


Fig. 5.3. Plot of log k versus $1/T$ for the reaction $2HI \rightarrow H_2 + I_2$.

Changing equation (5.16) into exponential form, we get:

$$k = A'e^{-B/T} \tag{5.17}$$

From equation (5.17), it is clear that the rate constant, k, will increase exponentially with increase in temperature, T (Fig. 5.4).

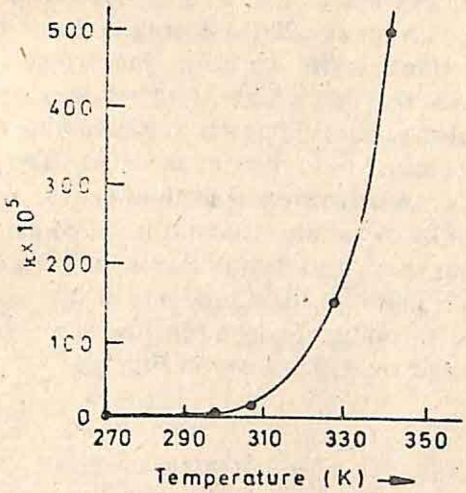


Fig. 5.4 Variation of k with temperature for the decomposition of N_2O_5.

Arrhenius further interpreted the above equation as:

$$k = A\,e^{-E_a/RT} \tag{5.17}$$

where E_a is the activation energy for the reaction, A is related to the number of binary molecular collisions per second per litre and is called the *frequency factor* (or *Arrhenius factor*) and R is a gas constant.

ENERGY BARRIER AND ACTIVATED COMPLEX

All molecules do not have the same energy at the same temperature. Collisions, which result in a chemical change, occur between those molecules which possess a certain minimum energy. This minimum energy is called the *threshold energy*.

Many reactions do not occur at room temperature but can be made to take place at higher temperature. This is due to the fact that none of the reactants in such a case possesses threshold energy at room temperature. Therefore no effective collisions take place. Increase in temperature supplies enough energy to the reactant molecules to make them acquire threshold energy and the reaction starts.

We have said that the colliding molecules do not react unless they possess threshold energy required to make the collision effective. In order to attains, the threshold energy, the colliding molecules must possess the activation energy, E_a, over and above the average energy. This energy of the reactant molecules is furnished by the kinetic energy associated with molecular collisions. Collisions occurring with an associated energy of E_a or greater can result in chemical reactions. After collision, the molecules loaded with the energy E_a pass through a high energy state where the bonds of the reacting molecules are supposed to loosen and new loose bonds of the product molecules appear to exist. The structure of the molecules in this *transition state* resembles neither the reactants nor products. Such intermediate structure is called ***activated complex.*** This exists as transitory and unstable species. Once formed, it will decompose very quickly to form products or the original reactants. A plot of the potential energy as a function of progress of reaction will give a curve of the type shown in Fig. 5.5.

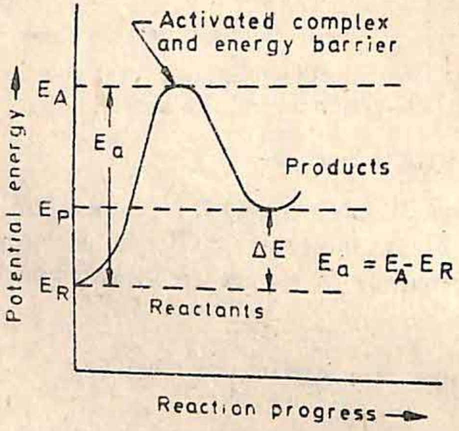


Fig. 5.5. Plot of potential energy versus reaction path of a system.

The activated complex is just like an ***energy barrier*** placed between the reactants and the products in a chemical reaction. If the colliding molecules have sufficient energy so as to reach the peak, they can go to the right side of the slope and change into products (Fig. 5.5). If the molecules collide with insufficient energy, they will not be able to reach the peak of the barrier and come back to the initial stage. Thus this barrier determines the threshold energy for the reacting molecules to cross the barrier and react. The excess energy that the reactants in the original state must absorb to get activated (fom activated complex) and then react is known as *activation energy*.

If the original reactants have the energy E_R and the products have the energy E_P, the difference of these two ($\triangle E$) is the energy change accompanying the reaction. Thus:

$$E_P - E_R = \triangle E$$

It is clear from Fig. 5.6, if E_R is greater than E_P, the reaction is exothermic. For endothermic reactions, E_P is greater than E_R. It is important to note that the heat absorbed or released is independent of the activation energy of the process. The activation energy is required by the reactants to cross the energy barrier.

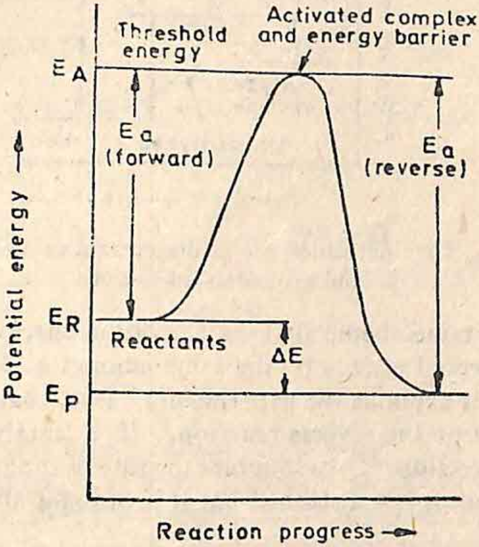


Fig. 5.6 Potential energy barrier for an exothermic reaction.

Catalyst

Many reactions proceed quite slowly when the reactants are mixed alone but can be made to occur much more rapidly by the introduction of other substances. These substances are called *catalysts* and are not used up in the reaction. In a reversible reaction, a catalyst speeds both the forward reaction and the backward reaction so that the equilibrium is established very soon. It does not disturb the equilibrium state at all.

When a catalyst is added, a new reaction path is opened up with a different energy barrier (Fig. 5.7). The solid curve shows the activation energy barrier which must be overcome for the reaction to occur. The new reaction path in presence of a catalyst is shown as a dashed curve. The catalyzed route possesses a lower activation energy than the original non-catalyzed path. This new reaction path corresponds to a different activated complex. Thus, more particles can get over the new *lower* energy barrier and the rate of reaction is increased.

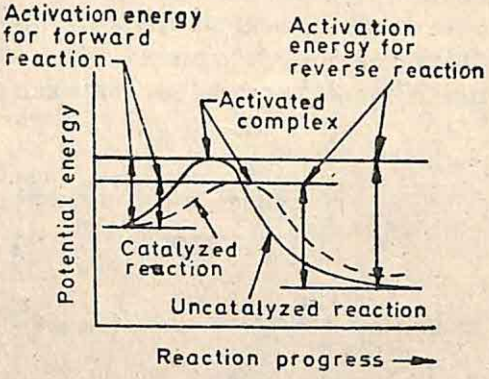


Fig. 5.7. Activation energy diagram for catalyzed and non-catalyzed reations.

It must be remembered that the activation energy for the reverse reaction is lowered exactly by the same amount as for the forward reaction. This explains the experimental fact that a catalyst has an equal effect on the reverse reaction. If a catalyst doubles the rate in one direction, it also doubles the rate in the reverse direction. The equilibrium is not disturbed but it is brought about in a shorter time.

The functio of a catalyst is to split up the main reaction into two or more steps. The potential energy barrier for each step is smaller than that for the single step of the main reaction. In other words, the catalyst helps to cross the barrier in two or more steps.

There are two main types of catalytic reactions: Homogeneous and heterogeneous.

HOMOGENEOUS CATALYTIC REACTIONS

Here the reactants and the catalysts are in the same phase. Some examples are:

Combination of SO_2 and O_2 to form SO_3 is catalyzed by gaseous NO

$$2SO_2(g)+O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

Synthesis of HCl is catalyzed by water vapour

$$H_2(g)+Cl_2(g) \xrightarrow{H_2O(g)} 2HCl(g)$$

Hydrolysis of ester takes place faster in presence of acid or alkali.

$$CH_3COOCH_3(l)+H_2O(l) \xrightarrow{H^+(l) \text{ or } OH^-(l)} CH_3COOH(l)+CH_3OH(l)$$

HETEROGENEOUS CATALYTIC REACTIONS

Here the reactants and the catalysts have different phases. For example:

$$CO(g)+H_2O(g) \xrightarrow{Fe_2O_3(s)} CO_2(g)+H_2(g)$$

$$CH_4(g)+H_2O(g) \xrightarrow{Ni(s)} CO(g)+3H_2(g)$$

$$C_2H_4(g)+\tfrac{1}{2}O_2(g) \xrightarrow{Ag(s)} C_2H_4O(g)$$

$$N_2(g)+3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

$$\text{Unsaturated oil }(l)+H_2(g) \longrightarrow \text{Saturated fat }(s)$$

$$2SO_2(g)+O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$$

Radiation

Some chemical reactions proceed only under the influence of light radiation which provides the necessary energy to overcome the energy barrier and start the reaction. For example, hydrogen and chlorine combine, and silver halides decompose on exposure to light. Such reactions which take place by means of light radiation are called photochemical reactions. Photons with energy ($E=h\nu$) provide the necessary activation energy for the molecules to react. The sequence of steps in combination of hydrogen and chlorine may be written as:

Initiation reaction

$$Cl_2+h\nu \longrightarrow 2Cl^{\cdot}$$

Provagation reaction

$$Cl^{\cdot}+H_2 \longrightarrow HCl+H^{\cdot}$$

$$H^{\cdot}+Cl_2 \longrightarrow HCl+Cl^{\cdot}$$

Chain termination reaction

$$M+H^{\cdot}+H^{\cdot} \longrightarrow M+H_2$$

$$M+Cl^{\cdot}+Cl^{\cdot} \longrightarrow M+Cl_2$$

Cl· and H· are very reactive species and are known as free radicals. M is the third (inert) body on which the recombination of atoms takes place.

5.8. REVERSIBLE REACTIONS

These are the reactions in which the products of the reaction can be brought back into the reactants. For example:

When steam reacts on iron, it gives Fe_3O_4 and hydrogen

$$3Fe+4H_2O \longrightarrow Fe_3O_4+4H_2$$

when hydrogen is passed over heated Fe_3O_4, it gives iron and steam.

$$Fe_3O_4+4H_2 \longrightarrow 3Fe+4H_2O$$

Thus these two reactions are reversible and can be written as under by using ($\rightleftharpoons$) sign in place of the usual single arrow sign.

$$3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$$

More examples of reversible reactions are:

$$H_2+I_2 \rightleftharpoons 2HI$$
$$2SO_2+O_2 \rightleftharpoons 2SO_3$$
$$N_2+O_2 \rightleftharpoons 2NO$$
$$N_2O_4 \rightleftharpoons 2NO_2$$

Consider a reaction which is unimolecular from both sides and is in equilibrium:

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

$$\text{Rate of forward reaction} = k_f\, A \qquad (5.18)$$

$$\text{Rate of reverse reaction} = k_r\, B \qquad (5.19)$$

where k_f and k_r are the rate constants for the forward and reverse reactions, respectively.

At equilibrium, rate of forward reaction is equal to that of reverse reaction:

$$k_f[A]=k_r[B]$$
$$k_f=k_r$$
$$\frac{[B]}{[A]}=\frac{k_f}{k_r}=K \qquad (5.20)$$

where K is ealled the *equilibrium constant* and equation (5.20) is known as the *law of chemical equilibrium.*

5.9. ENZYME CATALYSIS

Enzymes are complex non-living nitrogenous compounds present in living micro-organsims, both plants and animals. Their characteristics are:

(i) They are colloidal in nature.
(ii) They act as catalysts.
(iii) Their catalytic action is specific, *i.e.*, one enzyme can bring about only one particular reaction.
(iv) The enzymes have a specific temperature at which their activity is maximum. This temperature is known as *optimum temperature*.
(v) Each enzyme is associated with a *co-enzyme* which may increase its efficiency.
(vi) Enzymes are destroyed by ultraviolet rays, H_2S, HCN and antiseptics like arsenic and mercury salts.

Mechanism of Enzyme Catalysis

The enzyme (E) reacts with the molecule of a reactant called *substrate* (S) and forms a complex:

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substrate}}{S} \rightleftharpoons \underset{\text{Complex}}{ES}$$

The complex then breaks into products:

$$\underset{\text{Complex}}{ES} \longrightarrow \underset{\text{Enzyme}}{E} + \underset{\text{Product}}{P}$$

The lock and key type relationship for enzyme action is shown in Fig. 5.8. Enzymes bring about the reactions at body temperature which otherwise require much higher temperature.

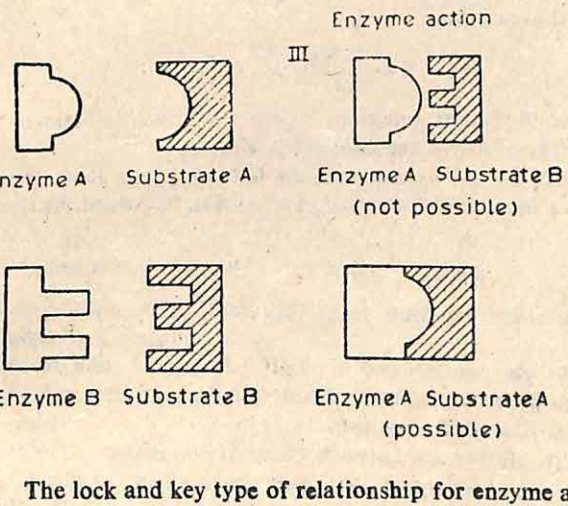


Fig. 5.8. The lock and key type of relationship for enzyme action.

Some examples of enzyme catalysis are:

The enzyme *urease* catalyzes the hydrolysis of urea

$$H_2N-CO-NH_2+H_2O \xrightarrow{\text{Urease}} 2NH_3+CO_2$$

Invertase brings about the hydrolysis of sugar to glucose and fructose.

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

Zymase converts glucose to alcohol

$$\underset{\text{Glucose}}{C_6H_{12}O_6}+H_2O \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH}+2CO_2$$

Lactic bacili present in curd catalyzes the fermentation of milk. The enzyme *lipase* catalyzes the fermentation of sugar to produce glycerol.

EXERCISES

5.1 What do you understand by chemical kinetics? Give examples of fast and slow reactions.

5.2 Define rate of a reaction. Explain its relation to the concentration of reactants.

5.3 Derive an expression for rate equation and explain the significance of terms involved.

5.4 Derive the equation:

$$k=\frac{2.303}{t}\log\frac{a}{a-x}$$

for a unimolecular reaction, where a is the initial concentration and x is the number of moles decomposed in time t.

5.5 For the reaction A→ products, the following data were obtained at 298 K (C_A represents the concentration of A in mol lit^{-1}) present at time t:

t (sec)	0	5	10	20	30
C_A	0.461	0.371	0.298	0.196	0.123

Show that the reaction is of the first order and find the value of rate consant. (Ans. $k=0.0434$ sec^{-1} average)

5.6 What do you understand by half life period of a reaction? How is it related to the rate constant? Using the data given in exercise 5.5, calculate the half period of the reaction. (Ans. *1.97* seconds)

5.7 Explain the differences between order and molecularity of a reaction.

5.8 Briefly discuss the important factors which affect the rate of a reaction.

5.9 How does temperature affect the rate of a reaction? How is this effect explained by the concept of threshold energy.

5.10 Discuss the concept of activated complex.

5.11 How do the nature and concentration of reactants affect the rate of reaction?

5.12 Discuss the role of a catalyst on the basis of activation energy.

5.13 Catalyst provides a a different reaction path and lowers the activation energy. Explain.

5.14 Write short notes on:

(i) Activation energy.	(ii) Reversible reactions.
(iii) Homogeneous catalysis.	(iv) Heterogeneous catalysis.

5.15 Give two examples of reactions which are influenced by radiation.

5.16 Give the mechanism of enzyme catalysis. Describe a few applications of enzyme catalysts.

Unit 6

Solutions

Ideal and non-ideal solutions. Colligative properties of dilute solutions of non-electrolytes (osmotic pressure, elevation of boiling point and depression in freezing point; derivation of equations not required). Measurement of osmotic pressure. Calculation of molecular masses. Abnormal molecular masses.

Solutions are homogeneous mixtures of two or more components having uniform properties such as density, refractive index, etc. They can exist in gaseous, liquid or solid states. The most common and the most important are the liquid solutions. In this Unit, we shall study some aspects of the solutions, particularly liquid solutions.

6.1. TYPES OF SOLUTIONS

After mixing the components, the solution can be solid, liquid or gaseous in form. Before we classify the solutions, let us understand the terms *component*, *solvent* and *solute*.

The substances used to make up a solution are known as components. One of the components which is present in large amount and is usually in the same physical state as the solution, is called the solvent. The other component present in less amount is known as solute. The solvent of a solution is the substance which acts as the dissolving medium. The solute of a solution is the substance dissolved. Sometimes the terms solvent and solute are used somewhat arbitrarily. In cases where both substances are liquids and present in approximately the same proportions, one is justified to fix up either of the components as the solvent or the solute. In a solution of ethyl alcohol and water, either liquid can be designated as the solvent. As can be seen from Table 6.1 classifying solutions, solvent or solute can be from any state of matter—gaseous, liquid or solid.

TABLE 6.1

Solute	*Solvent*	*Example*
Gas	Gas	Any mixture of gases as in air
Gas	Liquid	Mineral water, aerated drink (CO_2 in H_2O)
Gas	Solid	Adsorbed gas in mineral or metal like hydrogen in palladium
Liquid	Gas	Water vapour in air
Liquid	Liquid	Alcohol in water, benzene in toluene, carbon disulphide in carbon tetrachloride
Liquid	Solid	Liquid mercury in zinc or gold
Solid	Gas	Iodine vapour in air, camphor in air
Solid	Liquid	Sugar in water, common salt in water
Solid	Solid	Alloys like brass containing zinc in copper

In gaseous solutions (for example, air), gases form homogeneous mixtures and thus all gas mixtures are solutions. Unlike gases, all liquids do not mix with each other. Liquid pairs can be *miscible*, *partially miscible* or *immiscible*. Miscible liquids are those which are completely soluble in each other, *e.g.*, water and ethyl alcohol. Partially miscible liquids (such as water and ether) show a limited solubility in each other, while immiscible liquids (such as oil and water mixture) have no mutual solubility.

Chemically alike liquids dissolve in one another more freely as compared to others. Alkanes, for example, are miscible in all proportions because their molecules are alike. However, they do not dissolve in water because they cannot break hydrogen bonding in water molecules. Ethyl alcohol and water are completely miscible in each other because both of them are capable of forming hydrogen bonds through the ^-OH groups which they contain. Mutually soluble liquids usually have their molecules of approximately same size. Dipole-dipole interactions also play a significant role in forming liquid solutions.

The rule of 'like dissolves like' is applicable to solids. Thus polar solids (ionic compounds) dissolve in polar solvents such as water, alcohol or liquid ammonia than the non-polar ones like alkanes, benzene, ether, etc.

Chemical similarity and closeness of molecular sizes play important role in obtaining solid solutions, i.e., solutions in the solid state. Gold and copper form a solid solution because gold atoms can replace copper atoms in copper crystal and copper atoms can replace gold atoms in the gold crystal.

6.2. MODES OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

The relative amount of a solute to solvent in a solution is the *concentration* of the solution. The concentration can be expressed in several ways :

Mole fraction

It is the ratio of moles of one component to the total number of moles of the components (solute as well as solvent) of a solution. Considering that the solution is prepared from two components, A and B, we have:

$$\text{Mole fraction of A} = \frac{\text{Moles of A}}{\text{Moles of A} + \text{Moles of B}}$$

$$\text{Mole fraction of B} = \frac{\text{Moles of B}}{\text{Moles of A} + \text{Moles of B}}$$

In a solution containing one mole of water and three moles of alcohol, we have:

$$\text{Mole fraction of water} = \frac{\text{Mole of water}}{\text{Mole of water} + \text{Moles of alcohol}}$$

$$= \frac{1}{1+3} = \frac{1}{4} = 0.25$$

$$\text{Mole fraction of alcohol} = \frac{\text{Moles of alcohol}}{\text{Mole of waier} + \text{Moles of alcohol}}$$

$$= \frac{3}{1+3} = \frac{3}{4} = 0.75$$

Molarity, M

The molarity of a solution is the number of moles of the solute per litre of the solution. A 0.1 M solution of KCl means that one litre of such a solution contains 0.1 mole of KCl. A 0.2 M solution of $CuSO_4.5H_2O$ contains 0.2 mole of $CuSO_4.5H_2O$ per litre of the solution.

Molality, m

The molality of a solution is the number of moles of the solute per

1000 g (1 kg) of the solvent. A 1 m solution of glucose contains 1 mole of glucose in 1000 g of water. A 5 m solution of hydrochloric acid means that it has been prepared by dissolving 5 moles of HCl in 1000 g of water.

Normality, N

The normality of a solution is the number of gram-equivalents of solute per litre of the solution. A 0.1 N $K_2Cr_2O_7$ solution means that it contains 0.1 gram-equivalent of $K_2Cr_2O_7$ per litre of the solution. A 0.5 N $CuSO_4.5H_2O$ solution contains 0.5 gram-equivalent of $CuSO_4.5H_2O$ per litre of the solution. The amount in gram-equivalent may vary from reaction to reaction.

Parts per million, ppm. It is used when the concentration of a substance in solution is very small. It may be expressed as:

$$\text{ppm of a substance} = \frac{\text{Mass of the substance}}{\text{Total mass}} \times 10^6$$

Thus 1 g of NaCl, if dissolved in a total mass of one million grams (*i.e.*, 10^6 g), it will form a solution containing 1 ppm of NaCl.

$$\text{ppm of NaCl} = \frac{\text{Mass of NaCl}}{\text{Total Mass}} \times 10^6 = \frac{1}{10^6} \times 10^6 = 1$$

Per cent of solute may refer to per cent by weight or per cent by volume. Thus, 5% NaCl *by weight* would represent 5 g of NaCl in 100 g of solution. A 10% alcohol *by volume* would be a solution obtained from 10 ml of alcohol in a total volume of 100 ml.

6.3. VAPOUR PRESSURE OF SOLUTIONS

In a solution of two miscible liquids, A and B, the partial vapour pressure, P_A, of liquid A will be proportional to its mole fraction, χ_A. Similarly, the partial vapour pressure, P_B, of liquid B will be proportional to its mole fraction, χ_B. Thus,

$$P_A \propto \chi_A$$

$$\text{or } P_A = P_A^\circ \chi_A$$

$$\text{Also } P_B \propto \chi_A$$

$$\text{or } P_B = P_B^\circ \chi_B$$

where P_A° and P_B° are the proportionality constants and refer to vapour pressures of pure components A and B, respectively. This relationship was given by Francois Raoult in 1886 and is known as *Raoult's law*. It states: *For a solution of volatile liquids, the pressure of any component is equal to the product of the vapour pressure of the pure component and the mole fraction of that component in solution.*

Thus, according to Raoult's law, a plot of P_A against x_A should give a straight line passing through P_A° when $x_A=1$ (shown by broken line I in Fig. 6.1). Similarly, a plot of P_B versus x_B should give a straight line passing through P_B° when x_B equals unity (broken line II in Fig. 6.1). The total vapour pressure, P, exerted by the solution as a whole is the sum of P_A and P_B (shown in Fig 6.1 by line III joining the points P_A° and P_B°). The solutions which obey Raoult's law are called *ideal solutions.*

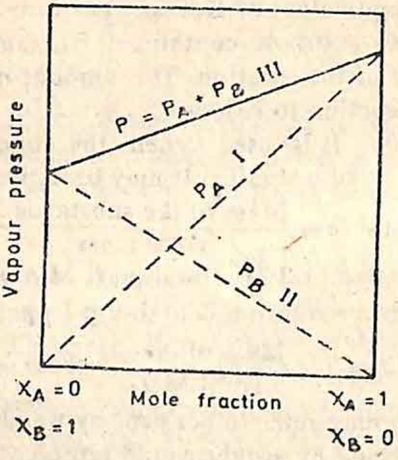


Fig. 6.1. Partial and total vapour pressure curves for solutions that follow Raoult's law.

If a solution contains a non-volatile solute, say for example sugar in aqueous solution, there is practically no contribution of solute to the total vapour pressure of the solution. Its pressure is only due to solvent.

Thus, $P=P_A=x_A P_A^\circ=P_A^\circ(1-\chi_B)$ (since $x_A+x_B=1$)

or, $\frac{P_A}{P_A^\circ}=1-\chi_B$

Rearranging, we obtain $1-\frac{P_A}{P_A^\circ}=\chi_B$

Hence, $$\frac{P_A^\circ-P_A}{P_A^\circ}=x_B \qquad (6.1)$$

The expresssion, $\frac{P_A^\circ-P_A}{P_A^\circ}$, denotes the relative lowering of vapour pressure on formation of solution. Thus for a solution of non-volatile solute, Raoult's law can be stated as: *The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute when solvent alone is volatile.*

6.4. IDEAL SOLUTIONS

A solution which obeys Raoult's law is referred to as *ideal solution*. The properties of such a solution are the average of the properties of its components in proportion to their mole fractions.

In ideal solution, the molecules of the two mixing components have similarity in shape and size. The molecular interactions between the components in the solution are of the same type as those which operate between the molecules of each component in the pure state. Thus, a solution containing A and B will be ideal only if the intermolecular attractive forces between A and A, B and B, and A and B are all alike. Such a solution can form when the components are identical in structure and polarity. Liquids like benzene and toluene form nearly ideal solution when mixed together in any proportion. This is because attractions between benzene-benzene, toluene-toluene and benzene-toluene are almost alike. The other examples of solutions exhibiting practically the ideal behaviour are provided by the mixtures of *n*-hexane and *n*-heptane, ethyl bromide and ethyl iodide, and chlorobenzene and bromobenzene, etc.

On mixing the components in an ideal solution, there will neither be a volume change (*i.e.*, $\Delta V=0$) nor enthalpy change (*i.e.*, $\Delta H=0$) because of no change in intermolecular attractive forces of the components. Thus, if we mix 20 ml of a solute with 80 ml of a solvent, the total volume of the resulting ideal solution will be 100 ml (*i.e.*, $\Delta V=0$). Also, no heat will be absorbed or evolved (*i.e.*, $\Delta H=0$). Thus, an ideal solution is one that obeys Raoult's law over the entire range of concentration and which can be prepared from its components involving neither volume change (*i.e.*, $\Delta V=0$) nor ethalpy change (*i.e.*, $\Delta H=0$).

Few solutions are ideal. However, as the concentration of the solute decreases, the solution becomes increasingly ideal. This is because most molecules of the solvent remain surrounded by similar solvent molecules. Thus, all dilute solutions are almost ideal.

6.5. NON-IDEAL SOLUTIONS

A non-ideal solution does not obey Raoult's law. Its formation is also accompanied by volume change and enthalpy change. Most of the miscible liquid-pairs form non-ideal solutions, *i.e.*, they deviate from Raoult's law. The deviation can be positive or negative.

Positive Deviation

This type of deviation is shown by liquid-pairs for which A-B attractive forces are weaker than the A-A or B-B attractive forces. In such a case, A as well as B find it easier to escape from the solution and thus partial pressures of both A and B, and the total vapour pressure become higher than predicted (Fig. 6.2) from the Raoult's law. An example of such a solution is of ethanol-cyclohexane mixture. In pure ethanol molecule, there is hydrogen bonding. When cyclohexane is added to ethanol, the molecules of cyclohexane get in between the ethanol molecules, break the hydrogen bonds and thus reduce the ethanal-ethanol intermolecular forces. As expected, such a liquid pair showing positive deviation will show a slight increase in volume and absorption of heat on mixing the components.

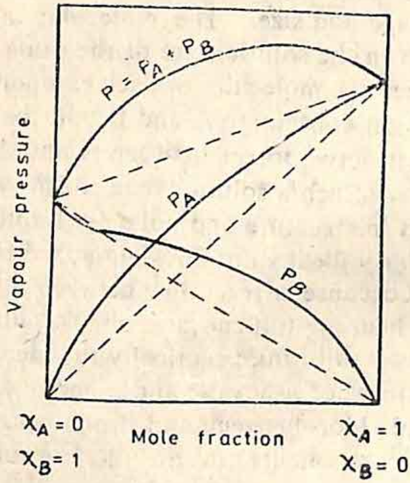
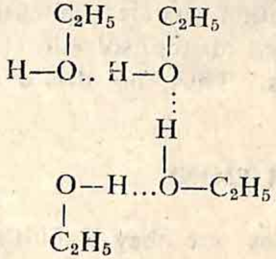


Fig. 6.2. Partial and total vapour pressure curves for solutions that show positive deviations from Raoult's law.



Hydrogen bonding in ethanol.

Negative Deviation

This type of deviation is shown by liquid-pairs for which A-B attractions are stronger than A-A or B-B attractions. Both A and

B find it more difficult to leave the solution and thus their partial pressures and the total vapour pressure become lower than predicted (Fig. 6.3). Such a solution will show an increase in boiling point on adding more of the solute. Negative deviation is shown by a mixture of acetone and chloroform. When they are mixed, hydrogen bonding takes place between them. This increases the acetone-chloroform intermolecular forces as is shown by evolution of heat and contraction in volume.

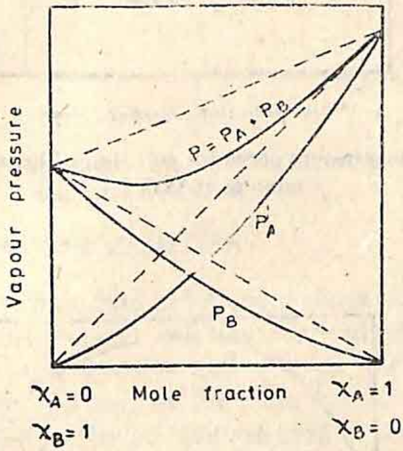
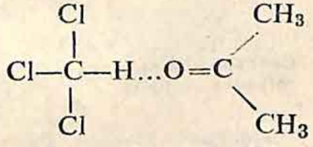


Fig. 6.3. Partial and total vapour pressure curves for solutions that show negative deviations from Raoult's law



Hydrogen bonding between chloroform and acetone

Vapour pressure plot obtained in case of benzene-toluene mixture at 353K is shown in Fig 6.4. As the solution nearly obeys Raoult's law, a straight line is obtained. From Fig. 6.5 it is evident that benzene-methanol mixture at 328K shows a positive deviation from Raoult's law. It means the polar benzene and non-polar methanol molecules prefer the company of their own kind.

Benzene-acetone, acetone-ethanol, carbon tetrachloride-toluene, etc., are some other examples of liquid pairs showing positive deviations. The negative deviation from Raoult's law shown by acetone-

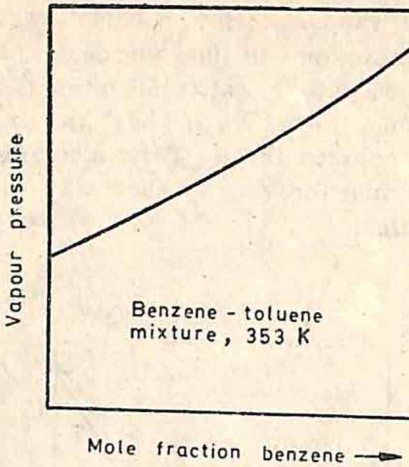


Fig. 6.4. Vapour pressure curve for solution of benzene-toluene mixture at 353K.

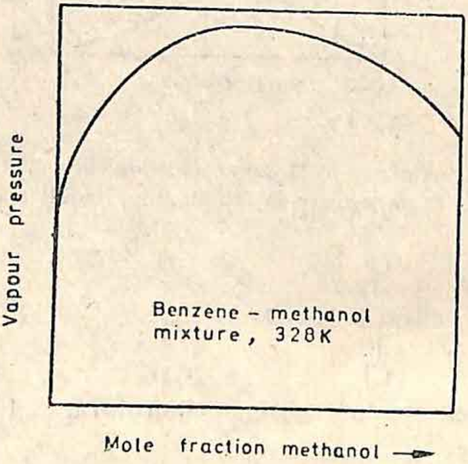


Fig. 6.5. Vapour pressure curve for solution of benzene-methanol mixture at 328K.

chloroform mixture at 308K is plotted in Fig. 6.6. It is clear that both liquids prefer company of each other to their own. Some more examples of liquid-pairs showing negative deviations are provided by water-hydrochloric acid, water-nitric acid, chloroform-benzene, etc.

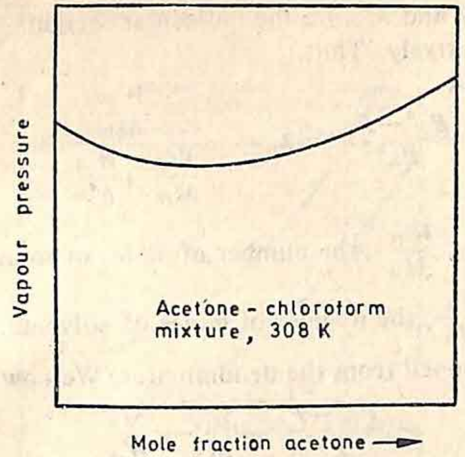


Fig. 6.6. Vapour pressure curve for solution of acetone-chloroform mixture at 308K.

6.6. COLLIGATIVE PROPERTIES

We have learnt that dilute solutions behave as ideal solutions and certain properties of such solutions depend only on the mole fraction of the solute species and not on their nature. These properties which depend only on the mole fraction of the solute are known as *colligative properties* and are used in the determination of molecular masses of substances. Some important colligative properties are:

(i) Relative lowering of vapour pressure.
(ii) Elevation of boiling points.
(iii) Depression of freezing points.
(iv) Osmotic pressure.

Relative Lowering of Vapour Pressure

In section 6.3, we have derived the expression:

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \chi_B$$

It shows that the relative lowering of vapour pressure is related to the mole fraction of the solute and not to its nature,

$$\text{now, } \chi_B = \frac{n_B}{n_A + n_B} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

Where n_A and n_B are the number of moles, W_A and W_B are the weights and M_A and M_B are the molecular weights of components A and B, respectively. Thus,

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \chi_B = \frac{\dfrac{W_B}{M_B}}{\dfrac{W_A}{M_A} + \dfrac{W_B}{M_B}} \tag{6.2}$$

In dilute solution, $\frac{W_B}{M_B}$, the number of moles of solute, is negligible compared to $\frac{W_A}{M_A}$, the number of moles of solvent. The term $\frac{W_B}{M_B}$ can thus be dropped from the denominator. We now obtain,

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} \tag{6.3}$$

The above expression can be used to determine the molecular mass of the solute B for a solution of known concentration if we measure the relative lowering of vapour pressure and also know the molecular mass of A.

Elevation of Boiling Points

The normal boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. Since the vapour pressure of a solvent at any given temperature is lowered by the addition of solute, it becomes necessary to heat the solution to a still higher temperature before the solution boils, *i.e.*, before its vapour pressure equals the atmospheric pressure. In other words, the boiling point of a solvent is always raised by the presence of a non-volatile solute or the solution boils at a higher temperature than the pure solvent.

In Fig. 6.7, AB is the vapour pressure curve for solvent and CD is the vapour pressure curve for solution of a non-volatile solute at different temperatures. It is evident that the vapour pressure of the solution is lower than that of the solvent at all temperatures. At temperature T_1, the vapour pressure of the pure solvent (shown by B) becomes equal to the atmospheric pressure. Thus T_1 is the boiling point of the solvent. The vapour pressure of the solution at T_1 is much less as shown by point E in the diagram. The vapour pressure in this case becomes equal to the atmospheric pressure (point D) only when the temperature is raised to T_2. Thus T_2 is the boiling point of the solution. The solution, therefore, boils at a temperature higher than that of the pure solvent. Evidently, the difference of the two temperatures, $T_2 - T_1$, is the elevation of the boiling point. Let us represent it by ΔT_b. Since its magnitude is

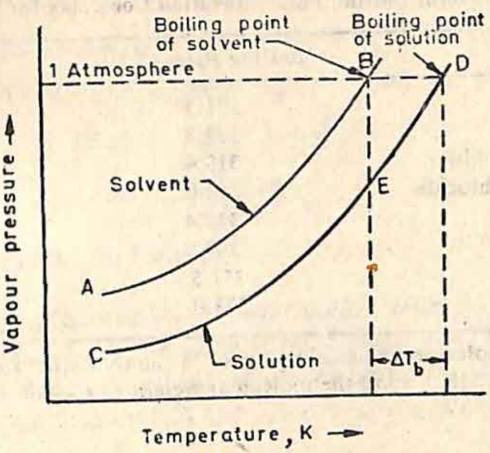


Fig. 6.7. Vapour pressure curves of a pure solvent and a solution of non-volatile solute (elevation of boiling point of a solution).

determined by that of the vapour pressure lowering, ΔT_b is also proportional to the solute concentration. Thus,

$$\Delta T_b \propto \varkappa_B$$

$$\text{or} \quad \Delta T_b = K.\varkappa_B \tag{6.4}$$

where K is a proportionality constant.

From equations (6.2) and (6.3), we know:

$$\varkappa_B = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\text{or} \quad \varkappa_B = n_B \times \frac{M_A}{W_A} \qquad \left(\text{Since } n_B = \frac{W_B}{M_B}\right) \tag{6.5}$$

Substituting equation (6.5) in (6.4), we get:

$$\Delta T_b = K.n_B.\frac{M_A}{W_A}$$

If we take the mass of the solvent, W_A, in kg, the term $\frac{n_B}{W_A}$ becomes molality, m, of the solution (molality is the number of moles of the solute per kg of solvent). Thus,

$$\Delta T_b = K.M_A.m = k_b m \tag{6.6}$$

where k_b is the new proportionality constant and is called the *molal boiling point elevation constant* for the solvent. It may be defined as the elevation in boiling point of a solution containing 1 gram mole of a solute per kilogram of the solvent. Different solvents have their characteristic k_b values. In Table 6.2, k_b values (expressed as degree/molality, *i.e.*, k/m) of some solvents are given.

TABLE: 6.2: Molal Boiling Point Elevation Constants for Some Solvents

Solvent	*Boiling Point* (K)	k_b (K/m)
Acetic acid	391.3	3.07
Benzene	353.3	2.53
Carbon disulphide	319.4	2.34
Carbon tetrachloride	350.0	5.03
Chloroform	334.4	3.63
Ether	307.8	2.02
Ethyl alcohol	351.5	1.20
Water	373.0	0.52

Example 6.1. A solution containing 2 g of a non-volatile solute in 20 g of water boils at 373.52K. Find the molecular weight of the solute (k_b for water =0.52 K/m).

Solution

$$\Delta T_b = 373.52 - 373.0 = 0.52\text{K}$$
$$k_b = 0.52\text{ K/m}$$

Putting these values in the expression: $\Delta T_b = k_b\text{m}$

$$0.52 = 0.52 \times \text{m}$$
$$\text{or} \quad \text{m} = 1$$

Now, 20 g of water solvent contains 2 g of non-volatile solute or $\frac{2}{M_B}$ mole of the solute (where M_B is the molecular weight of the solute). It means 1000 g of the solvent will contain $\frac{2}{M_B} \times \frac{1000}{20} = \frac{100}{M_B}$ moles of the solute. This is also equal to the molality, m, of the solution.

$$\text{Thus,} \quad m = 1 = \frac{100}{M_B}$$
$$\text{or} \quad M_B = 100$$

Example 6.2. A solution containg 1.20 g of an organic solute per 50 g of CCl_4 boils at 350.5K under atmospheric pressure. What is the molecular mass of the solule? Normal boiling point of CCl_4 is 350.0 and its k_b value is 5.0K/m.

Solution

$$\Delta T_b = 350.5 - 350.0 = 0.50\text{K}$$
$$k_b = 5.0\text{ K/m}$$

Substituting these values in the expression: $\Delta T_b = k_b\text{m}$

$$0.50 = 5.0 \times \text{m}$$
$$\text{or} \quad \text{m} = \frac{0.5}{5.0} = 0.1$$

Now, 50 g of CCl_4 solvent contains 1.20 g of solute or $\frac{1.20}{M_B}$ mole of the solute (where M_B is the molecular mass of the solute). It means 1000 g of the solvent will contain $\frac{1.20}{M_B} \times \frac{1000}{50} = \frac{24}{M_B}$ moles of the solute. This is also equal to the molality, m, of the solution.

$$\text{Thus,} \qquad m = 0.1 = \frac{24}{M_B}$$

$$\text{or} \quad M_B = 240$$

Depression of Freezing Points

Freezing point of a substance is that temperature at which its solid and liquid phases have the same vapour pressure. If a non-volatile solute is dissolved in a solvent, the freezing point of the solution is lowered compared to that of the solvent as is shown in Fig. 6.8.

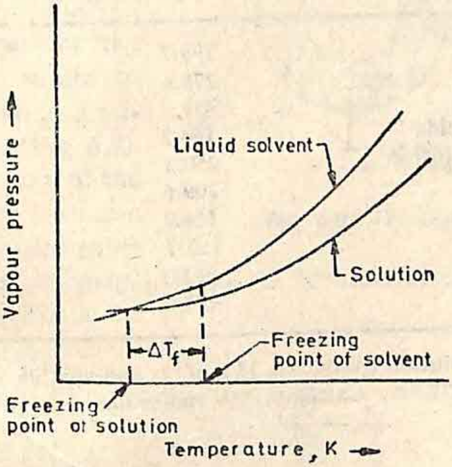


Fig. 6.8. Vapour pressure curves of a pure solvent and a solution of a non-volatile solute (depression of freezing point of a solution).

The lowering observed at the freezing point (denoted by ΔT_f) is also found to be proportional to the mole fraction of the solute. Thus,

$$\Delta T_f \propto x_B$$

$$\text{or} \quad \Delta T_f = K . x_B \tag{6.7}$$

where K is a proportionality constant.

From equation (6.5), we know $x_B = n_B \times \frac{M_A}{W_A}$

Equation (6.7) takes the form:

$$\Delta T_f = K.n_B.\frac{M_A}{W_A}$$

If we take mass of the solvent, W_A, in kg the term $\frac{n_B}{W_A}$ becomes molality, *m*, of the solution. Thus,

$$\Delta T_f = K.M_A.m = k_f m \tag{6.8}$$

where k_f is the *molal freezing point depression constant* or *molal cryoscopic constant* for the solvent. It is defined as the depression in freezing point of a solution containing 1 gram mole of a solute per kilogram of the solvent. Each solvent possesses a characteristic value of k_f. Table 6.3 lists k_f values for some solvents.

TABLE 6.3: Molal Freezing Point Depression Constants for Some Solvents

Solvent	*Freezing point* (K)	k_f (K/*m*)
Acetic acid	289.7	3.90
Benzene	278.6	5.12
Camphor	452.0	39.70
Carbon disulphide	164.2	3.83
Carbon tetrachloride	250.5	31.80
Chloroform	209.6	4.70
Ether	156.9	1.79
Ethyl alcohol	155.7	1.99
Naphthalene	353.3	6.80
Water	273.0	1.86

Example 6.3. A solution containing 18 g of a non-volatile solute in 200 g of water freezes at 272.0K. Calculate the molecular mass of the solute (k_f= 1.86 K/m).

Solution

$$\Delta T_f = 273.00 - 272.07 = 0.93\text{K}$$

$$k_f = 1.86\ \text{K/m}$$

Substituting these values in the expression: $\Delta T_f = k_f \text{m}$

$$0.93 = 1.86 \times \text{m}$$

$$\text{or} \quad \text{m} = \frac{0.93}{1.86} = 0.5$$

Now, 18 g of water (solvent) contains 18 g of solute or $\frac{18}{M_B}$ mole of the solute (where M_B is the molecular mass of the solute). It means 1000 g of the solvent will contain $\frac{18}{M_B} \times \frac{1000}{200} = \frac{90}{M_B}$ moles of the solute. This is also equal to the molality of the solution. Thus,

$$m = 0.5 = \frac{90}{M_B}$$

$$\text{or} \quad M_B = \frac{90}{0.5} = 180$$

Osmotic Pressure

When a solution of a solute and the pure solvent are separated from each other by a special membrane such as that of cellophane or parchment, the movement of the solute particles from the solution into the solvent is prevented but the flow of the solvent into the solution continues. Such a membrane which permits the solvent but not the solute to pass through it is called *semipermeable membrane* (Fig. 6.9). The process of the flow of the pure solvent into solution through a semipermeable membrane is known as *osmosis*. It can be demonstrated by a simple apparatus shown in Fig. 6.10.

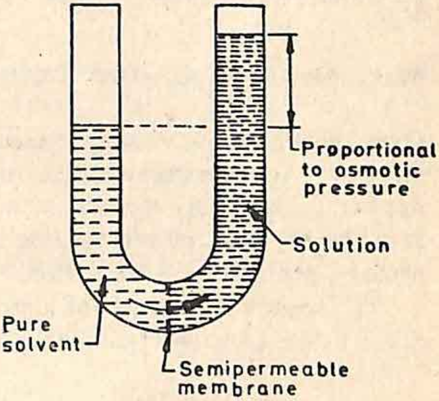


Fig. 6.9. Osmosis.

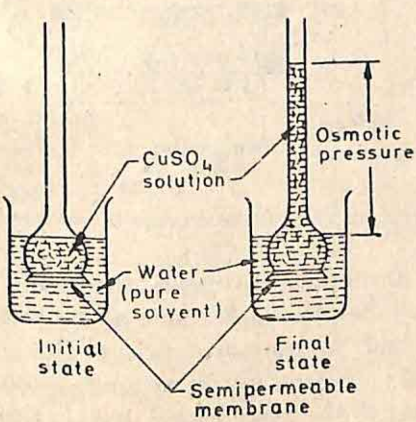


Fig. 6.10. Demonstration of osmosis and osmotic pressure.

Take some copper sulphate solution in an inverted thistle funnel, the mouth of which is covered with a semipermeable membrane. Lower the funnel into a beaker containing water solvent. A considerable rise in level of the solution in the funnel will be noticed. After some time, the level of the solution will acquire a definite maximum value. When this happens, the hydrostatic pressure of the column is just sufficient to stop the inward flow of the solvent into the solution. This hydrostatic pressure, since it is produced by the process of osmosis, is termed as *osmotic pressure* of the solution. The osmosis can be checked by applying a mechanical pressure on the solution equal to its osmotic pressure.

MEASUREMENT OF OSMOTIC PRESSURE

Osmotic pressure is usually measured by the method of Berkley and Hartley. It consists in measuring the external or counter pressure applied to the solution mechanically which is just sufficient to prevent the entry of the solvent into solution. This corresponds to the osmotic pressure of the solution.

The apparatus consists of a strong vessel into which a porous pot is fitted (Fig. 6.11). The walls of the pot are deposited with a semipermeable membrane of copper ferrocyanide. The pot is fitted with a capillary indicator on one side and a water reservoir on the other. Water and solution are taken in the pot and in the vessel, respectively. Due to osmosis, water tends to flow from the pot into the solution through the membrane. It is indicated by the fall in water level in the capillary indicator. This flow or osmosis of water into the solution can be stopped by the application of external pressure on the solution with the help of a piston and the level in the

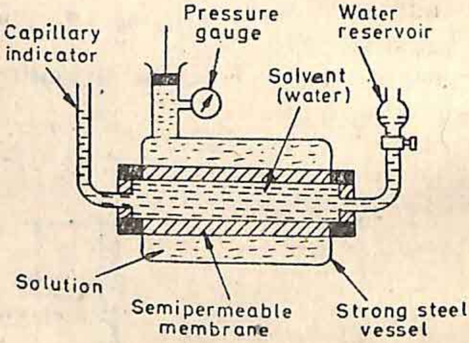


Fig. 6.11. Determination of osmotic pressure (Berkley and Hartley method).

capillary tube is maintained. The pressure so applied is equal to the osmtic pressure and is indicated by the pressure gauge.

Osmotic pressure (denoted by π), like the other colligative properties, is also related to the mole fraction, x_B, of the solute. Thus,

$$\pi \propto x_B$$

$$\pi = Kx_B \tag{6.9}$$

where K is a proportionality constant.

It can be shown that for v litres of solution containing n_B moles of solute, the osmotic pressure is given by:

$$\pi = \frac{n_B}{v} RT \tag{6.10}$$

where R is a constant equal to the gas constant (=0.08205 litre atm deg^{-1} mol^{-1}) and T is the absolute temperature. The above expression is called *van't Hoff's solution equation* or *vant's Hoff osmotic pressure formula.* It is used to calculate osmotic pressures of solutions.

Example 6.4. What will be the osmotic pressure of a solution containing 6 g of urea per litre at 300 K ? Molecular weight of urea is 60.

Solution

$$\pi = \frac{n_B}{v} RT = \frac{6/60}{1} \times 0.082 \times 300 = 2.46 \text{ atm}.$$

6.7. MOLECULAR MASSES FROM COLLIGATIVE PROPERTIES

Colligative properties of solutions, as we have discussed, are used to determine the molecular masses of non-volatile substances like proteins, polymers, sugars, etc. The depression of freezing point method is more commonly employed because the change in freezing point is larger than the change in boiling point for a solution. For example, k_f and k_b values for water are 1.86 and 0.52, respectively.

In the Beckmann method of the measurement of $\triangle T_f$, the apparatus shown in Fig. 6.12 is used. The freezing bath is adjusted to a temperature slightly lower than the freezing point of the pure solvent. The solutions are slightly supercooled and are momentarily stirred to break up the supercooling. The highest temperature reached thereafter is taken as the freezing point. We will now solve

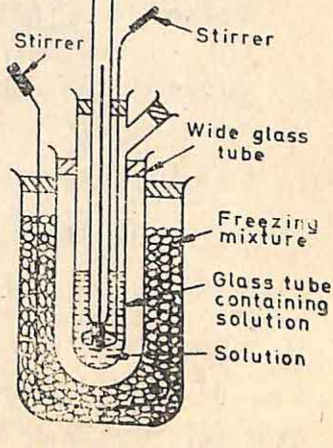


Fig. 6.12. Apparatus for determination of $\triangle T_f$ (Beckmann method).

some more numericals to show how the colligative properties are useful in calculating the molecular masses.

Example 6.5. A solution prepared from 0.3 g of an unknown non-volatile solute in 30.0 g CCl_4 boils at 350.392K. Calculate the molecular weight of the solute. The boiling point of CCl_4 and its k_b values are 350.0K and 5.03, respectively.

Solution

We know, $\Delta T_b = k_b m$

Now, $\Delta T_b = 350.392 - 350.0 = 0.392$

$k_b = 5.03$

Substituting these values in the expression, we obtain:

$$m = \frac{\Delta T_b}{k_b} = \frac{0.392}{5.03} = 0.0779$$

Now, 30.0 g of CCl_4 contains 0.3 g of the solute or $\frac{0.3}{M_B}$ mole of the solute (where M_B is the molecular weight of the solute). Thus, 1000 g of CCl_4 will contain $\frac{0.3}{M_B} \times \frac{1000}{30} = \frac{10}{M_B}$ moles of the solute. This, again, is equal to m of the solution. So, we can write:

$$m = 0.0779 = \frac{10}{M_B}$$

or $$M_B = \frac{10}{0.0779} = 128$$

Example 6.6. Osmotic pressure of a solution containing 6 g of dissolved protein per 100 ml of the solution is 0.0329 atm at 310 K. What is the molecular mass of the protein? The value of R is given to be 0.08205 litre atm $deg^{-1} mol^{-1}$

Solution

We know, $\pi = \frac{n_B}{v} RT$

Now, $\pi = 0.0329$ atm; $n_B = \frac{6}{M_B}$; $v = 100$ ml $= 0.1$ litre; $R = 0.08205$;

$T = 310$ K

Substituting these values in the expression, we get:

$$0.0329 = \frac{6/M_B}{0.1} \times 0.08205 \times 310$$

or $$M_B = \frac{6 \times 0.08205 \times 310}{0.1 \times 0.0329} = 46387$$

6.8. ABNORMAL MOLECULAR MASSES

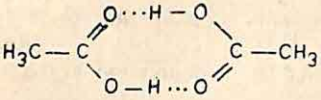
Sometimes the molecular masses determined by the colligative properties are different from the normal values. This is due to:

(i) Association of solute molecules or

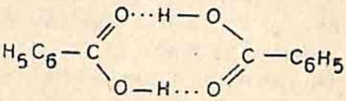
(ii) Dissociation of solute molecules.

The *association* of solute particles leads to a decrease in the number of molecular particles on dissolving them in a solvent. It results in a decrease in the values of colligative properties and consequently the higher values are obtained for molecular masses.

The association is found to be generally due to hydrogen bonding between molecules. Alcohols, phenols, carboxylic acids, etc., are capable of forming hydrogen bonds. For example, acetic acid dissolved in benzene shows a mass of 120 (normal molecular mass is 60). Similarly, benzoic acid dissolved in benzene shows double of its normal molecular mass This is explained by hydrogen bonding when a dimer is obtained in each case.



Acetic acid dimer



Benzoic acid dimer

In case of *dissociation* of solute particles (as it happens in solutions of strong electrolytes like strong acids, bases and salts), the number of effective species increases in the solvent. This results in proportionately increased values of colligative properties and thereby lower values are obtained for molecular masses. For example, if we have equimolar solutions of salt and sugar in water, the former will have a larger osmotic pressure than the latter. Consequently, the observed molecular mass of the salt will be lowered.

To account for the abnormal molecular masses, van't Hoff (1886) introduced a factor, *i* known as *van't Hoff constant*. It expresses the degree of association or dissociation and can be written as:

$$i=\frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

In case of association, *i*, is less than unity while it is more than unity in case of dissociation.

EXERCISES

6.1 What is meant by a solution? Explain the difference between a solute and a solvent.

6.2 Give the classification of solutions with appropriate examples.

6.3 What are the different methods of expressing the concentration of a solution?

6.4 What is the molarity of a 20.0% H_2SO_4 solution if its density is 1.14 g cm^{-3}? **(Ans. 2.32 M)**

6.5 Calculate the normality and molarity of a solution containing 30 g oxalic acid ($H_2C_2O_4.2H_2O$) per litre. **(Ans. 0.476 M 0.238 m)**

6.6 (i) Define molarity and molality of a solution.
(ii) Which is a more concentrated solution: **(Ans. 1 m)**
1 *M* or 1 *m*

6.7 What are ideal and non-ideal solutions?

6.8 State and explain Raoult's law.

6.9 What are positive and negative deviations in case of non-ideal solutions? Explain the causes of such deviations.

6.10 What are the colligative properties of solutions? On what factor do these properties depend?

6.11 Derive the relationship between elevation of a boiling point and molecular mass of a solute.

6.12 A solution contains 7 g of a non-volatile solute in 250 g of water and it boils at 373.52 K. Calculate the molecular mass of the solute (k_b for water=0.52 K/m). **(Ans. 56)**

6.13 How is molecular mass of a solute related to the depression in the freezing point?

6.14 A solution of 0.25 g of a substance in 25 g of benzene lowers the freezing point by 0.40 K. Calculate the molecular mass of the substance (k_f for benzene=5.12 K/m). **(Ans. 128)**

6.15 Why do solutes elevate the boiling point and depress the freezing point of a solvent?

6.16 Explain the terms osmosis and osmotic pressure. How does osmosis differ from osmotic pressure?

6.17 Write the expression for van't Hoff's solution equation. Give the significance of each term involved.

6.18 Calculate the osmotic pressure of a solution containing 34.2 g of cane sugar (molecular mass 342 g) in 1000 g of water at 300 K ($R=0.082$). **(Ans. 2.46 atm)**

6.19 Why do we obtain abnormal molecular masses in some cases by using colligative properties of the solution? Explain the significance of van't Hoff constant.

6.20 An aqueous solution contains 5 g of an organic substance per litre of the solution. Its osmotic pressure is found to be 0.59 atm at 280 K. Calculate the molecular mass of the substance. **(Ans. 194.6 g)**

Unit 7

Electrochemistry

Galvanic cells and cell and electrode potentials,
Electrochemical series.

In the study of electrolysis, we learnt that electrical energy can be used to bring about chemical changes. In this Unit, we shall learn more about electrochemistry and study galvanic or voltaic cells in which the chemical reactions are used to produce electrical energy.

7.1. REDOX REACTIONS

An *oxidizing agent* is that one which oxidizes another substance and in the process gains electrons. A *reducing agent*, on the other hand, loses electrons and reduces the other substance. Thus in a reaction between Cu^{2+} ions (oxidizing agent) and metallic zinc (reducing agent), the former gain electrons and oxidize zinc. In other words, zinc reduces Cu^{2+} ions and itself loses electrons.

$$\underset{\text{(Reducing agent)}}{Zn(s)} \longrightarrow Zn^{2+}(aq) + 2e^- \qquad \text{Oxidation}$$

$$\underset{\text{(Oxidizing agent)}}{Cu^{2+}(aq) + 2e^-} \longrightarrow Cu(s) \qquad \text{Reduction}$$

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad \text{Redox reaction}$$

The overall reaction, in which *red*uction and *ox*idation are coupled, is called *redox reaction*. Similarly in volumetric titration of Fe^{2+} with acidified $KMnO_4$, Fe^{2+} gets oxidized to Fe^{3+} and $KMnO_4$ is reduced to Mn^{2+}.

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^- \qquad \text{Oxidation}$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad \text{Reduction}$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \qquad \text{Overall redox reaction}$$

Such chemical changes involving redox reactions are used to produce electrical energy.

7.2. ELECTROCHEMICAL CELLS

Based on redox reactions, electrochemical cells are constructed to convert chemical energy into electrical energy. These cells are known as *galvanic* or *voltaic* cells. A voltaic cell in which one electrode is zinc placed in zinc sulphate solution and the other is copper in copper sulphate solution is called the *Daniell cell*. A schematic diagram of the cell is shown in Fig. 7.1. The two half-reactions, *i.e.*, $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ and $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, are made to take place simultaneously with the electron transfer occurring through an external conducting wire. The two solutions (*i.e.*, zinc sulphate and copper sulphate) are linked by an inverted U-shaped tube known as *salt bridge*. The tube is filled with a solution of an electrolyte such as KCl, KNO_3 or NH_4NO_3 to which gelatin or agar-agar has been added to obtain a semi-solid paste. Sometimes, instead of a salt bridge, a porous partition is used which separates the two solutions. This is less efficient but a more practical method is employed in the commercial form of Daniell cell (Fig. 7.2).

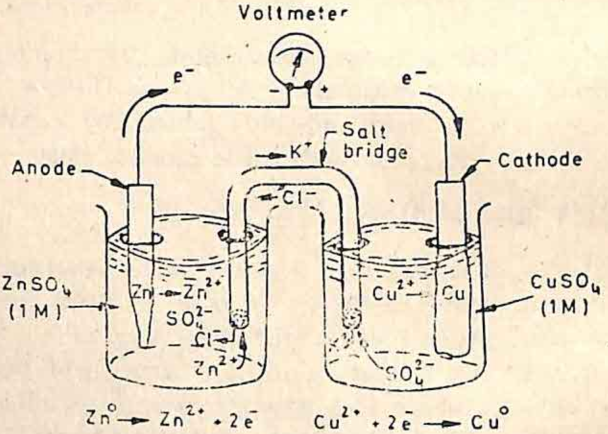


Fig. 7.1. Daniell cell.

The cell operation : At the zinc electrode, electrons and Zn^{2+} ions are produced by the *oxidation half-cell reaction :*

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e$$

The electrode which 'pushes' electrons into the external circuit is considered to be the *negative pole* or *anode* of the cell. Oxidation takes place here. The Zn^{2+} ions migrate away from the anode into the solution and the zinc rod loses weight.

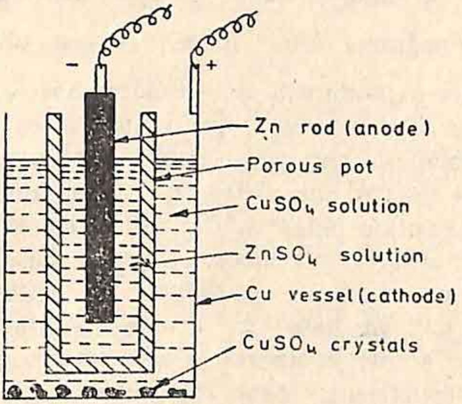


Fig. 7.2. Commercial form of Daniell cell.

The electrons produced by the above reaction move through the external wire into the copper electrode where they are picked up and are used in reducing Cu^{2+} ions in the solution to copper atoms. The *reduction half-cell reaction* is represented as:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

The copper electrode which 'pulls' electrons out of the external circuit is considered to be the *positive pole* or *cathode* of the cell. Copper ions thus get deposited after reduction on the copper rod which gains weight. Reduction occurs here.

The two half-cell reactions when combined give the net reaction of the cell:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

The number of electrons lost by zinc remains equal to the number of electrons gained by Cu^{2+}. The circuit gets completed and the solutions in the anode and cathode compartments maintain their electrical neutrality by migration of the ions of the salt bridge. The net effect of the two half-cell reactions is that electrons are forced into the external circuit at the anode and withdrawn from it at the cathode. This causes current to flow, or, if current is prevented from flowing by a device such as the voltmeter (Fig. 7.1), an electrical potential difference (voltage) is built up.

7.3. FUNCTION OF SALT BRIDGE

The transference of electrons from zinc anode to copper cathode leads to a net positive charge around the anode due to release of Zn^{2+} ions and a net negative charge around the cathode due to deposition of Cu^{2+} ions as Cu(s) on the cathode. The positive charge collected around the anode will prevent electrons to flow from it and the negative charge (due to excess of SO_4^{2-} ions) collected around the cathode will prevent acceptance of electrons from the anode. The reaction thus stops and no current will flow. The salt bridge comes to aid and restores electroneutrality of the two solutions in the two compartments. It contains a concentrated solution (concentration much higher than the solutions in the compartments) of an inert electrolyte, the ions of which are not involved in electrochemical reactions. The anions of the electrolyte (*e.g.*, Cl^- in case the bridge contains KCl, Fig. 7.1) migrate to the anode compartment and cations (*i.e.*, K^+ ions) to the cathode compartment. Thus, the bridge helps to prevent the accumulation of charges and maintains the flow of current.

7.4. OTHER GALVANIC CELLS

In principle, any redox reaction is separable into two half-cell reactions and can be used as a source of electric current in a galvanic cell. Some examples are given below :

$$Cu(s)+2Ag^+(aq) \longrightarrow Cu^{2+}(aq)+2Ag(s)$$
$$Ni(s)+Cu^{2+}(aq) \longrightarrow Ni^{2+}(aq)+2Cu(s)$$
$$Zn(s)+2Ag^+(aq) \longrightarrow Zn^{2+}(aq)+2Ag(s)$$

In each case, the apparatus consists of two half-cells, each containing an electrode dipping into a solution of an electrolyte of its own ions, separated by a salt bridge. Atoms of the element having greater tendency to lose electrons are oxidised at the anode, giving up electrons which travel through the external circuit to the cathode where they combine with the cations which are readily reduced. Thus in the first example, given above:

$$Cu(s) \longrightarrow Cu^{2+}(aq)+2e^- \text{ (Anode half-cell reaction, oxidation)}$$
$$2Ag^+(aq)+2e^- \longrightarrow 2Ag(s) \text{ (Cathode half-cell reaction, reduction)}$$

The overall reaction is the sum of the two half-cell reactions, *i.e.*,

$$Cu(s)+2Ag^+(aq) \longrightarrow Cu^{2+}+2Ag(s) \text{ (Overall redox reaction)}$$

The half-cell reactions take place simultaneously. The number of electrons released in one half-cell equals the number of electrons taken up in the other half-cell reaction.

7.5. CELL NOTATIONS

Certain notations have become fairly well known and followed conventionally in connection with electrochemical cells. A half-cell such as zinc rod immersed in 1.0 M Zn^{2+} solution is indicated as

$$Zn \mid Zn^{2+}(1.0\ M).$$

The verticle line shows a phase separation. The Daniel cell described in Fig. 7.1 may be designated as

$$Zn \mid Zn^{2+}(1.0\ M) \parallel Cu^{2+}(1.0\ M) \mid Cu$$

where the two vertical lines indicate the salt bridge.

By convention, the *anode* of a cell is shown on the *left* in the cell notation. Similarly, in the cell

$$Cd \mid Cd^{2+}(1.0\ M) \parallel Ag^{+}(1.0\ M) \mid Ag$$

Cd^{2+}/Cd electrode, shown on the left, is the anode of the cell.

7.6. ELECTRODE POTENTIALS

As it has been mentioned earlier that a voltmeter can be introduced between the two half-cells to measure the build up electrical potential difference (voltage). This potential difference is known as the *electromotive force* (abbreviated as emf or EMF) of the cell. The contribution of each electrode to the cell potential is called the *electrode potential*. The potential of a single electrode cannot be measured because when the second metal is dipped into the electrolyte to make the measurement, the metal becomes another electrode. Thus, we select one electrode arbitrarily as a standard and measure the *potential difference* between this standard electrode and any other electrode. By general convention (IUPAC recommendation), *normal hydrogen electrode* (abbreviated as NHE) is taken as the standard reference electrode. Its standard electrode potential has been assumed to be zero volt. The NHE consists of hydrogen gas at one atmosphere pressure in contact with 1 M solution of H^+ ions at all temperatures. A platinum electrode coated with platinum black is inserted into the assembly which catalyzes the attainment of equilibrium between the hydrogen gas and H^+ ions in the solution (Fig. 7.3). Potentials of all other electrodes are found by coupling with NHE.

A pure metal dipped in one molar solution of one of its ions (or in case a gas is involved, it is at a partial pressure of one atmosphere), is referred to as the *standard electrode.* When such an electrode is coupled with NHE, the measured potential is called the *standard electrode potential.* The symbol E is used to denote cell and electrode potentials; and $E°$ for standard electrode potentials.

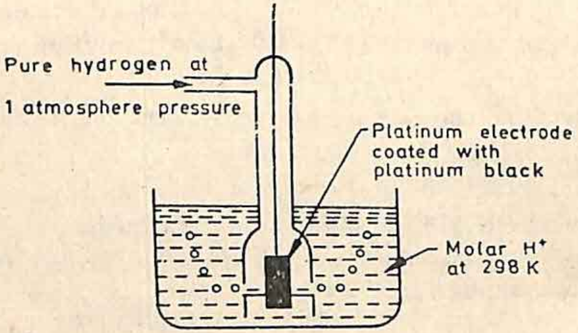


Fig. 7.3. Normal hydrogen electrode.

When coupled wilh NHE, some electrodes undergo spontaneous oxidation and permit reduction of NHE. For example, zinc electrode when combined with NHE is oxidized to Zn^{2+} ions. In other words, the zinc electrode pushes electrons into the external circuit and forms the anode. By convention, the anode is shown on the left (Fig. 7.4) and it is said to possess a negative value of ***reduction electrode potential.*** In case the electrode coupled with

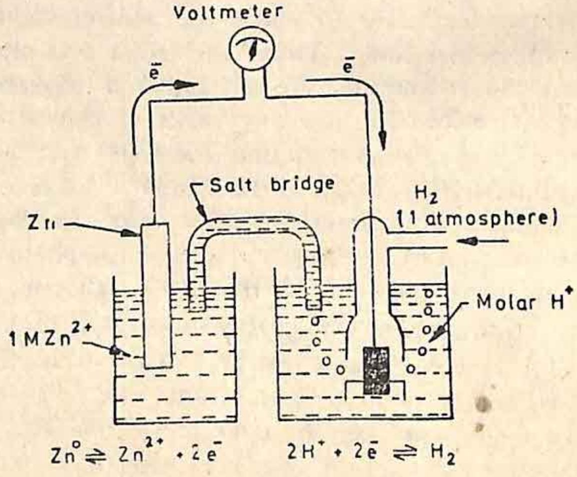

Voltmeter
$\bar{e}$
$\bar{e}$
Salt bridge
Zn
H_2
(1 atmosphere)
Molar H$^+$
1 M Zn^{2+}
$Zn° \rightleftharpoons Zn^{2+} + 2\bar{e}$
$2H^+ + 2\bar{e} \rightleftharpoons H_2$

Fig. 7.4. Zinc electrode acts as the anode when it is connected to NHE.

NHE undergoes spontaneous reduction, it allows oxidation of NHE. For example, when copper electrode dipped in Cu^{2+} solution is coupled with NHE, Cu^{2+} ions are reduced to Cu(s) and NHE is oxidized to H^+ ions. The copper electrode thus accepts electrons from the external circuit (Fig. 7.5) and it is said to have positive value of reduction electrode potential.

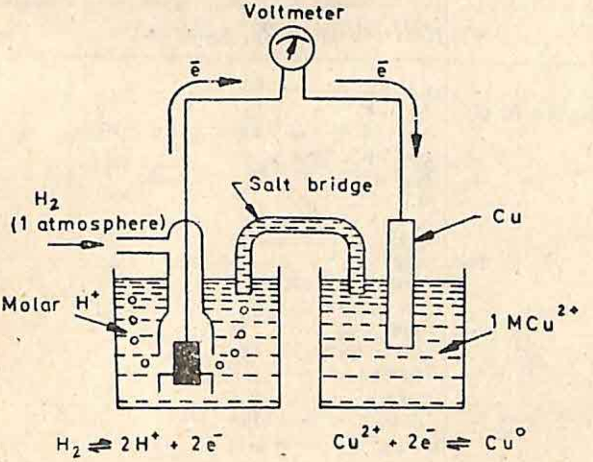


Fig 7.5. Copper electrode acts as the cathode when it is connected to NHE.

7.7. ELECTROCHEMICAL SERIES

Table 7.1 lists some half-cell reactions and their reduction potentials. The table is so arranged that the oxidizing agents are listed in increasing order of their strength and reduction potential. For example, Li^+ is the poorest oxidizing agent (and lowest reduction potential of -3.05 V) and F_2 is the best oxidizing agent (highest $E^\circ = +2.87$ V). This table giving the various substances in increasing order of reduction potential is called the *activity series or electrochemical series*. It may also be noted that the forward reaction for electrode potential is a reducing one, therefore, the E° values are known as the *standard reduction potentials*.

The oxidation and reduction processes can be predicted on the basis of E° values of electrochemical series. A given ion in the series will oxidize all the metals above it and a given metal will reduce the ions of all metals below it. For example, one can predict from the emf values of $Sn^{2+}|Sn$ and $Pb^{2+}|Pb$ electrodes (though there is only a slight difference in the values) that Sn° will displace Pb^{2+} ions from solution.

$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \qquad E^\circ = -0.13 \text{ V}$$
$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \qquad E^\circ = -0.14 \text{ V}$$

Subtracting: $Pb^{2+}(aq) + Sn(s) \rightleftharpoons Sn^{2+}(aq) + Pb(s)$

$$\triangle E^\circ = -0.13 - (-0.14) = +0.01 \text{ V}$$

TABLE 7.1 : Standard Electrode (Reduction) Potentials at 298K

(Electro-chemical Series)

Electrode	*Half-cell reaction (reduction)*	E° *(volts)*
$Li^+\|Li$	$Li^+ + e^- \longrightarrow Li$	−3.05
$M^+\|M$ (M=K, Rb or Cs)	$M^+ + e^- \longrightarrow M$	−2.93
$Ba^{2+}\|Ba$	$Ba^{2+} + 2e^- \longrightarrow Ba$	−2.90
$Ca^{2+}\|Ca$	$Ca^{2+} + 2e^- \longrightarrow Ca$	−2.76
$Na^+\|Na$	$Na^+ + e^- \longrightarrow Na$	−2.71
$Mg^{2+}\|Mg$	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.38
$Be^{2+}\|Be$	$Be^{2+} + 2e^- \longrightarrow Be$	−1.70
$Al^{3+}\|Al$	$Al^{3+} + 3e^- \longrightarrow Al$	−1.66
$Zn^{2+}\|Zn$	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76
$Cr^{3+}\|Cr$	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.74
$Fe^{2+}\|Fe$	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
$Cd^{2+}\|Cd$	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.40
$Co^{2+}\|Co$	$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$Ni^{2+}\|Ni$	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.25
$Sn^{2+}\|Sn$	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Pb^{2+}\|Pb$	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.13
$H^+\|\frac{1}{2}H_2$	$H^+ + e^- \longrightarrow \frac{1}{2}H_2$	±0.00 (By definition)
$Sn^{4+}\|Sn^{2+}$	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15
$Cu^{2+}\|Cu$	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$\frac{1}{2}I_2\|I^-$	$\frac{1}{2}I_2 + e^- \longrightarrow I^-$	+0.54
$Fe^{3+}\|Fe^{2+}$	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$Ag^+\|Ag$	$Ag^+ + e^- \longrightarrow Ag$	+0.80
$\frac{1}{2}Br_2\|Br^-$	$\frac{1}{2}Br_2 + e^- \longrightarrow Br^-$	+1.07
$\frac{1}{2}Cl_2\|Cl^-$	$\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-$	+1.36
$Au^{3+}\|Au$	$Au^{3+} + e^- \longrightarrow Au$	+1.50
$MnO_4^-\|Mn^{2+}$	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.5
$\frac{1}{2}F_2\|F^-$	$\frac{1}{2}F_2 + e^- \longrightarrow F^-$	+2.87

The positive value of emf indicates that the reaction will take place in forward direction (i.e., Sn° will displace Pb^{2+} ions).

Again, let us see whether Zn° reduces Pb^{2+} ions or Pb° reduces Zn^{2+} ions

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^\circ = -0.76 \text{ V}$$
$$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s) \qquad E^\circ = -0.13 \text{ V}$$

Subtracting : $Zn^{2+}(aq) + Pb(s) \rightleftharpoons Pb^{2}(aq) + Zn(S)$

$$\triangle E^\circ = -0.76 - (-0.13) = -0.63 \text{ V}$$

Since emf is negative, it means that the reaction will take place in the backward direction (i.e., Zn° will displace Pb^{2+} ions).

7.8. NERNST EQUATION

In the galvanic cells, when the concentrations of the oxidized and reduced species are not in the standard states, the electrode potential, E, of such systems is given by the Nernst equation:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

where E°=standard potential of a given system, R=gas constant (8.314 $\text{JK}^{-1}\ \text{mol}^{-1}$), T=kelvin temperature (298K, the temperature at which E° are given), F=Faraday constant (96 500 C mol^{-1}) and n=number of electrons involved (gained or lost) in the half-cell reaction.

Substituting the values of the constants and converting natural logarithms to common logarithms, we get:

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{Ox}]}{[\text{Red}]}$$

Example 7.1. Calculate the half-cell potential at 298K for the reaction, $\text{Zn}^{2+}\ (\text{aq}) + 2e^- \longrightarrow \text{Zn (s)}$, if $[\text{Zn}^{2+}]=0.01$ M.

Solution From Nernst equation, we know;

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{Ox}]}{[\text{Red}]}$$

$$= -0.76 + \frac{0.059}{2} \log (0.01)$$

(since $E^\circ_{\text{Zn}^{2+}|\text{Zn}} = -0.76$, from Table 7.1; $[\text{Zn}^{2+}]=0.01$, given)

$$= -0.79 + (-0.059) = -0.819 \text{ V}$$

Example 7.2. Calculate the electrode potential of a $\text{Cu}^{2+}|\text{Cu}$ electrode in which the concentration of Cu^{2+} ions is 2.0 M.

Solution According to Nernst equation,

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{Ox}]}{[\text{Red}]}$$

Now, $E^\circ = +0.34$ (from Table 7.1); $[\text{Ox}]=[\text{Cu}^{2+}]=2$(given); $n=2$

Substituting these values in the equation, we obtain:

$$E = 0.34 + \frac{0.059}{2} (0.03010) = 0.349 \text{ V}$$

7.9. CALCULATION OF CELL POTENTIALS FROM ELECTRODE POTENTIALS

The potential of any cell (E_{cell}) can be readily calculated from the difference of reduction potentials of the two half-cell reactions involved in the cell. Following the usual notations in which anode is shown on the left hand side and cathode on the right, we can say:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{right}} - E_{\text{left}}$$

Example 7.3 Calculate the emf for the following cells:

(i) $\text{Zn} \mid \text{Zn}^{2+}\ (1.0\ \text{M}) \parallel \text{Cu}^{2+}\ (1.0\ \text{M}) \mid \text{Cu}$

(ii) $\text{Ni} \mid \text{Ni}^{2+}\ (1.0\ \text{M}) \parallel \text{Au}^{3+}\ (1.0\ \text{M}) \mid \text{Au}$

(iii) $Cr \mid Cr^{3+}\ (1.0\ M) \parallel Co^{2+}\ (1.0\ M) \mid Co$
(iv) $Ag \mid Ag^{+}\ (1.0\ M) \parallel Cu^{2+}\ (1.0\ M) \mid Cu$

Solution We know, $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$

Substituting the reduction potential values from Table 7.1, we obtain:

(i) $E^\circ_{cell} = +0.34-(-0.76)=1.10\ V$

(ii) $E^\circ_{cell} = +1.50-(-0.25)=1.75\ V$

(iii) $E^\circ_{cell} = -0.28-(-0.74)=0.46\ V$

(iv) $E^\circ_{cell} = +0.34-(+0.80)=-0.46\ V$

The positive values of emf (E°_{cell}) show that (a) Zn will act as anode and Cu as cathode in cell (i); (b) Ni will act as anode and Au as cathode in cell (ii) and (c) Cr will act as anode and Co as cathode in cell (iii). The negative E_{cell} in cell (iv) means that Ag cannot act as anode but will function as cathode. Copper will act as anode.

7.10. SOME ENERGY PRODUCING CELLS

A variety of voltaic cells like *dry cells*, *lead storage battery* and more recently *fuel cells* are of immense practical importance as energy producing devices. Dry cells find use in transistors, calculators, flashlights, hearing aids and many other instruments; lead storage battery in motor cars; and fuel cells (*e.g.*, H_2/O_2 fuel cell) in space mission programmes.

In a commonly used dry cell (Fig. 7.6), a moist paste of NH_4Cl, $ZnCl_2$ and MnO_2, is taken in a zinc metal container. The container acts as the anode and is lined with porous paper separating zinc

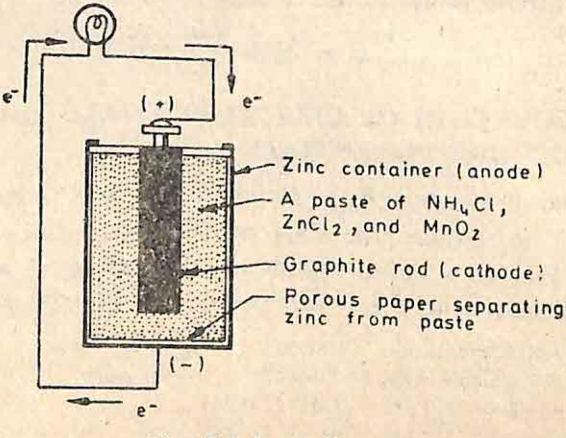

e⁻
(+)
e⁻
Zinc container (anode)
A paste of NH_4Cl, $ZnCl_2$, and MnO_2
Graphite rod (cathode)
Porous paper separating zinc from paste
(−)
e⁻

Fig. 7.6. Dry cell.

from the paste but permits ions to diffuse through it. A carbon or graphite cathode with a brass cap is placed in the centre of the container. The cap allows a better contact between the two electrodes. The oxidation reaction taking place at the anode can be represented as: $Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$

The electrons flow from zinc anode to carbon cathode when the two are connected. The NH_4^+ ions from the paste move towards cathode and remove the electrons. The reaction occurring at the cathode can be put as:

$$2NH_4^+\ (aq) + 2e^- + 2MnO_2\ (s) \longrightarrow Mn_2O_3\ (s) + H_2O(l) + 2NH_3\ (aq)$$

Ordinary dry cells cannot be recharged. In Ni-Cd based *rechargeable dry cells*, the electrode reactions may be summarized as:

At anode: $Cd\ (s) + 2OH^-\ (aq) \longrightarrow Cd\ (OH)_2\ (s) + 2e^-$

At cathode: $NiO_2\ (s) + 2e^- + 2H_2O\ (l) \longrightarrow Ni\ (OH)_2\ (s) + 2OH^-\ (aq)$

No gas is involved in the reactions. The reaction products remain adhering to the electrodes. The cells can, therefore, be recharged by converting back the reaction products.

EXERCISES

7.1 Define:
(i) Oxidation, (ii) Reduction,
(iii) Redox reaction, (iv) Voltaic cells.

7.2 What is meant by an electrochemical cell? Give suitable examples.

7.3 Describe the construction of Daniell cell and the reaction involved.

7.4 (i) What do you understand by oxidation half-cell reaction and reduction half-cell reaction?
(ii) Describe the role of a salt bridge.

7.5 Give the electrochemical conventions to express and formulate the cells.

7.6 Explain the following:
(i) Standard electrode potential.
(ii) Standard reduction potential.
(iii) Electromotive force.

7.7 Define cell potential. How is electrode potential determined from the cell voltage?

7.8 How are the half-cell reactions arranged in electrochemical series? Select the strongest oxidizing agent and the strongest reducing agent from the following: Li, Mg, Cu, Al, Cl_2, F_2.

7.9 With the help of Table 7.1, calculate $E°$ of the following cells:
(i) $Cd \mid Cd^{2+} \parallel Fe^{3+} \mid Fe^{2+}$
(ii) $Sn \mid Sn^{2+} \parallel Ag^+ \mid Ag$
(iii) $Al \mid Al^{3+} \parallel Cr^{3+} \mid Cr$

(Ans. (i) +1.17 V (ii) +0.94 V (iii) +0.92 V)

7.10 Calculate the electrode potential of a $Zn^{2+}|Zn$ electrode in which the concentration of Zn^{2+} ions is 0.1 M.

(Ans. −0.79 V)

7.11 What is Nernst equation? Explain the meaning of each term involved in the equation.

7.12 Referring E° values for the electrodes $Sn^{2+}|Sn$ and $Pb^{2+}|Pb$ in Table 7.1, calculate emf of the cell:

$$Sn \mid Sn^{2+} (1.0\ M) \parallel Pb^{2+}(0.001\ M)|Pb$$

Predict whether the cell will function or not.

(Ans. −0.079 V. The negative value implies that the cell cannot function in the manner shown but will operate in the reverse direction).

7.13 What is meant by normal hydrogen electrode? How is it used to determine the electrode potential?

7.14 Write short notes on the following:

(i) Daniell cell.
(ii) Dry cell.
(iii) Salt bridge.
(iv) NHE.

7.15 Construct diagram of the cell having the reaction

$$Ag^+ (1.0\ M) + Fe^{2+} (1.0\ M) \dashrightarrow Ag\ (s) + Fe^{3+} (1.0\ M)$$

E° values for $Ag^+|Ag$ and Fe^{2+} electrodes are +0.80 V and +0.77 V respectively. Also, calculate the emf of the cell. **(Ans. +0.03 V)**

Unit 8

Surface Chemistry

Adsorption of gases and solutes on solid surfaces. Colloidal state of matter, multimolecular and macromolecular colloids, preparation and characteristics (e.g. electrical, mechanical and optical) of colloids. Gold numbers, Emulsion and emulsifying agents.

When matter is finely divided, its surface is enormously increased and its properties undergo a variety of changes. The increased fraction of molecules present at or near the surface and the unbalanced distribution of the matter about them impart new characteristics to the surface. In this Unit, we shall discuss the chemistry related to the surface and study the phenomena like adsorption, colloidal state of matter, etc.

8.1. ADSORPTION

The molecules or ions present at the surface of a solid do not have all their forces (or valences) satisfied by union with other particles. As a result of this unsaturation, solid surfaces tend to satisfy their residual forces by attracting and retaining on them the molecules of other species which are brought into contact with them. As the molecules remain only at the surface and do not go deeper into the bulk, their concentration is more at the surface than in the bulk of the solid. The phenomenon of higher concentration of any molecular species on the surface than in the bulk of a solid is called *adsorption* (Fig. 8.1).

Adsorption may be distinguished from *absorption*. The latter term implies that molecules are uniformly distributed throughout the body of a solid. Thus, water vapour is absorbed by anhydrous

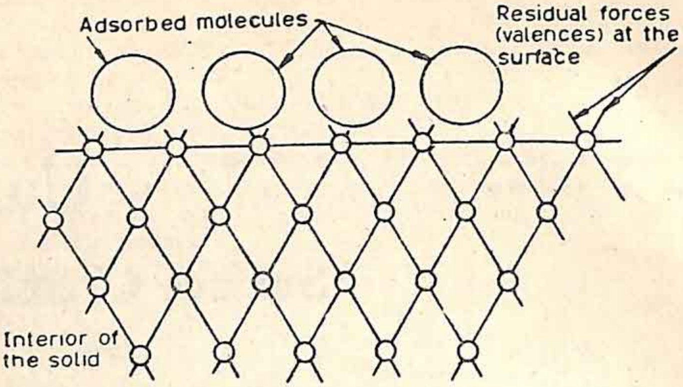


Fig. 8.1. Adsorption on the surface of a solid by residual forces (valences).

calcium chloride while it is adsorbed by silica gel. Similarly, while ammonia is absorbed in water, it is adsorbed by charcoal. The difference between absorption and adsorption is illustrated in Fig. 8.2.

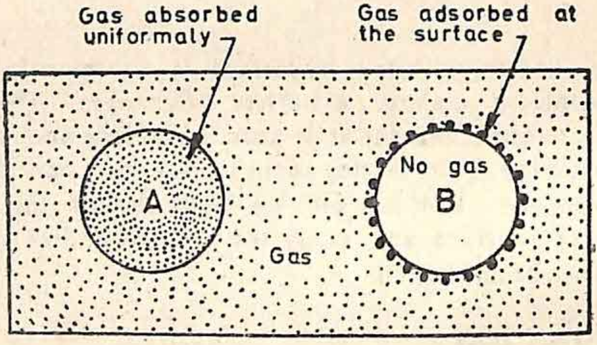


Fig. 8.2. Absorption and adsorption. Solid A has *absorbed* the gas uniformly. Solid B has *adsorbed* the gas at its surface.

The forces involved in adsorption are of various types such as van der Waals forces and even chemical bond forces. The material upon whose surface the adsorption takes place is called an *adsorbent* while the substance being adsorbed is called an *adsorbate*. The process of removal of an adsorbed substance from a surface on which it is adsorbed is known as *desorption*. The forces of adsorption come into existence as soon as a solid piece is broken into two to give two new surfaces (Fig. 8.3). In a complete piece of the solid, the available forces are used up to bind the constituent particles. In new surfaces, the forces left free act on particles of gases and of

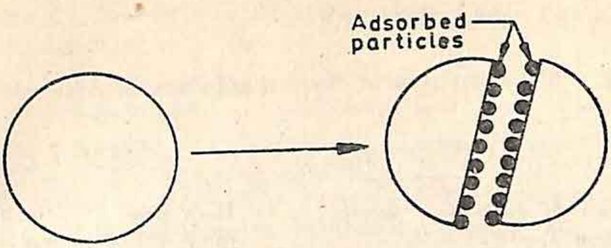


Fig. 8.3. Adsorption forces act when a solid is broken.

solutions. As a result, the particles get attracted and attached on the surfaces. This explains adsorption.

Types of Adsorption

Adsorption normally means increase in the concentration of adsorbate more at the surface as compared to its concentration in the bulk phase. This is called *positive adsorption*. Sometimes, in case of liquids, it is seen that the concentration of the solute is less at the surface layer than in the bulk part of the solution. This is also a case of adsorption due to difference in concentrations. Such an adsorption is called *negative adsorption*.

Adsorption may be classified according to the nature of binding forces. Thus:

PHYSICAL ADSORPTION

Here the adsorbate is held on a surface by van der Waals forces. It is also called *physisorption* or *van der Waals adsorption*. This type of adsorption is temporary and can be reduced by increasing the temperature or reducing the pressure of the gas.

CHEMICAL ADSORPTION

Here the adsorbate is held by forces which are as strong as in usual chemical bonding. It is also called *chemisorption* or *Langmuir adsorption*. Compared to physical adsorption, it is more permanent and may or may not be decreased by increasing the temperature or reducing the pressure.

Adsorption is accompanied by evolution of heat (exothermic). This is known as *heat of adsorption* or *enthalpy* and is equal to heat evolved for adsorption of one mole adsorbate on the surface of adsorbent. Heat of adsorption for chemisorption is more than that of physisorption. Table 8.1 lists differences between physical adsorption and chemical adsorption.

TABLE 8.1: Comparison of Physical and Chemical Adsorptions

	Physical adsorption	*Chemical adsorption*
1.	Low heat of adsorption usually in the range 20-40 kJ mol^{-1}.	High heat of adsorption in the range 40-400 kJ mol^{-1}
2.	Attraction due to van der Waals forces.	Attraction due to chemical bond forces.
3.	It usually takes place at low temperature and decreases with increasing temperature.	It takes place at high temperature.
4.	It is reversible in nature.	It is irreversible.
5.	It is approximately related to the ease of liquefaction of the gas.	It is independent of the liquefaction.
6.	It is not specific in nature.	It is often highly specific.
7.	It forms multimolecular layers.	Forms monomolecular layers.
8.	Rate of increase in adsorption with increase in pressure is much greater at higher pressures.	Rate of increase in adsorption with increase in pressure decreases.

8.2 ADSORPTION OF GASES ON SOLIDS

The amount of a gas absorbed by a solid depends on a number of factors as detailed below:

(i) Nature of Gas and Nature of Absorbent

It has been found that the more readily soluble and easily liquefiable gases such as NH_3, HCl, Cl_2 and SO_2 are adsorbed more than so called 'permanent' gases such as H_2, N_2 and O_2. The reason is that the van der Waals or molecular forces which are involved in adsorption are more predominant in the former category than in the latter cases.

Since adsorption is a surface phenomenon, it is evident that the greater the surface area per unit mass of the adsorbent, the greater is its capacity for adsorption under given conditions of temperature and pressure. Chemisorption is more specific in nature. A gas will be adsorbed only on such solids with which it can combine chemically.

Charcoal is a good adsorbent for easily liquefiable gases. Most of the poisonous gases belong to this type. This is why the gas masks containing charcoals of different types are used. Metals can adsorb hydrogen, oxygen and nitrogen. Adsorbents of large pores provide good adsorption for gases.

(ii) Effect of Temperature

As adsorption is accompanied by evolution of heat, so in accordance with Le-Chatelier's principle, the magnitude of adsorption should increase with fall in temperature and this is actually so. A graph drawn between the amount of substance adsorbed per gram (*x/m*) and temperature (*t*) at a constant pressure is called ***adsorption isobar***. The adsorption isobars for physical adsorption and chemisorption are shown in Fig. 8.4. They are different from each other. While a physical adsorption isobar shows a decrease in *x/m* as the temperature rises, isobar of chemisorption shows an increase in the beginning and then a decrease as the temperature increases. This initial increase is due to the fact that, like chemical reactions, chemisorption also requires activation energy.

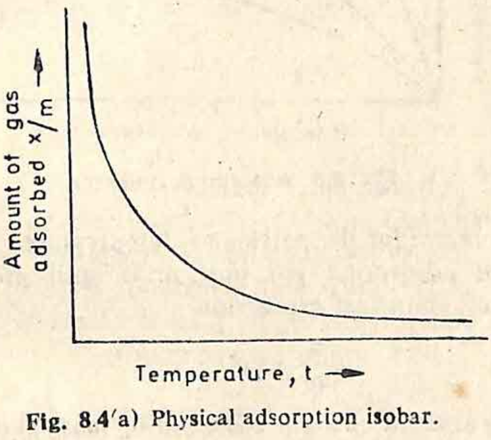


Fig. 8.4(a) Physical adsorption isobar.

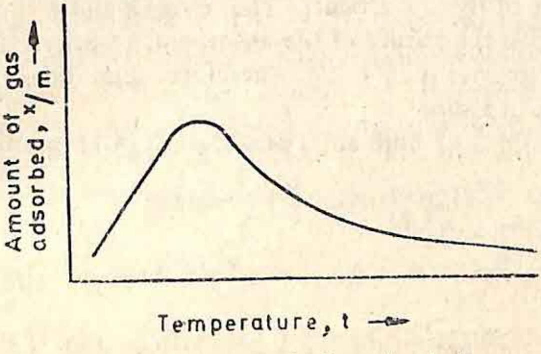


Fig. 8.4(b) Chemical adsorption isobar.

(iii) Effect of Pressure

Adsorption of a gas leads to a decrease of pressure. It follows that the magnitude of adsorption increases with increase in pressure. The variation of adsorption with pressure at a constant temperature is expressed graphically as in Fig. 8.5. The curve is known as *adsorption isotherm* for the particular temperature. The variation of amount of adsorption per unit mass with pressure is often expressed by an empirical expression:

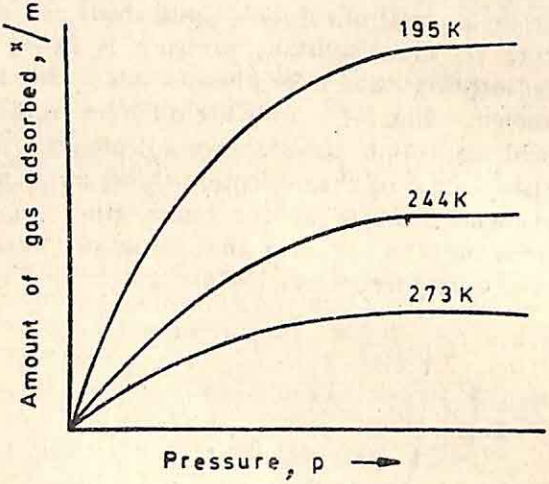


Fig. 8.5. Adsorption isotherm.

$$\frac{x}{m}=kp^{1/n} \tag{8.1}$$

where x is the amount of a gas adsorbed by mass m of the adsorbent at the pressure p, so that x/m denotes amount of the gas adsorbed per unit mass of the adsorbent. The terms n and k are constants depending upon the nature of the absorbent, adsorbate and temperature. As n is greater than 1 and, therefore, x/m does not rise as rapidly as the pressure.

Taking logarithms on both sides of equation (8.1), we obtain:

$$\log\frac{x}{m}=\log k+\frac{1}{n}\log p \tag{8.2}$$

Thus, a graph between $\log\left(\frac{x}{m}\right)$ and $\log p$ should give a straight line with an intercept on the $\log\left(\frac{x}{m}\right)$ axis equal to $\log k$ and the slope of the line equal to $\frac{1}{n}$ (Fig. 8.6). Equations (8.1) and (8.2) and the respective graphs in Figs. 8.5 and 8.6 are the different expressions of *Freundlich adsorption isotherms.*

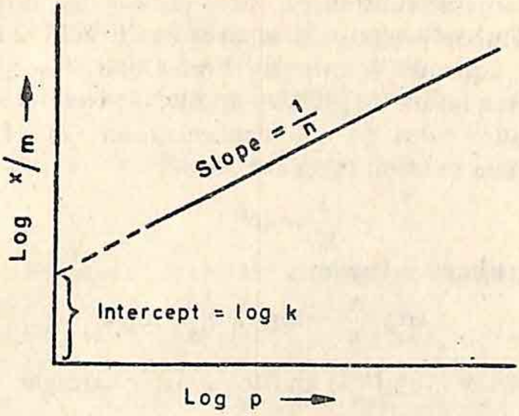


Fig. 8.6. Freundlich adsorption isotherm. A plot between $\log \frac{x}{m}$ and $\log p$.

(iv) Effect of Activation of the Adsorbent

The extent of adsorption can further be increased by 'activation' of the adsorbent in various ways. Thus, wood charcoal can be activated by heating between 650K and 1300K in vacuum, air or steam. The activation involves apparently a distilling out of hydrocarbon impurities from charcoal. This leads to exposure of a large free surface for a possible adsorption.

8.3. COMPETING ADSORPTION

Some adsorbates are adsorbed more than others. The following guidelines help us to know which substance will be adsorbed more:

(i) A more strongly adsorbable substance can replace an already adsorbed substance if the latter is adsorbed by weaker forces. For example, chlorine will be adsorbed over charcoal by displacing already adsorbed gases, present in air.

(ii) From a mixture of adsorbates, the more adsorbable may be adsorbed to a still greater extent than one could realize from its partial pressure. For example, moisture in air, though present to a small extent, is strongly adsorbed over silica gel. It is, therefore, used for drying air. Similarly, charcoal can more strongly adsorb polluting gases present in small amounts in air.

8.4. ADSORPTION OF SOLUTES FROM SOLUTIONS

Adsorbents are capable of adsorbing certain solutes from solutions. This property is made use of in adsorbing colouring matters from solutions of organic substances. Raw juice is decolorized by animal charcoal. Similarly, charcoal adsorbs oxalic acid and acetic acid from their aqueous solutions. Freundlich adsorption isotherm relationship (equation 8.1) is also applicable to solutions by replacing the pressure term by the concentration (*c*) of adsorbates in solutions. The relation takes the form:

$$\frac{x}{m} = kc^{1/n} \qquad (8.3)$$

Taking logarithms, it becomes:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c \qquad (8.4)$$

A graph between $\log (\frac{x}{m})$ and $\log c$ is a straight line for small ranges of concentrations.

8.5. APPLICATIONS OF ADSORPTION

The phenomenon of adsorption finds a large number of applications. A few examples are mentioned below:

(i) Chromatographic techniques depend on how well different compounds are adsorbed. Based on this, the adsorbed material is separated into different compounds (Fig. 8.7).

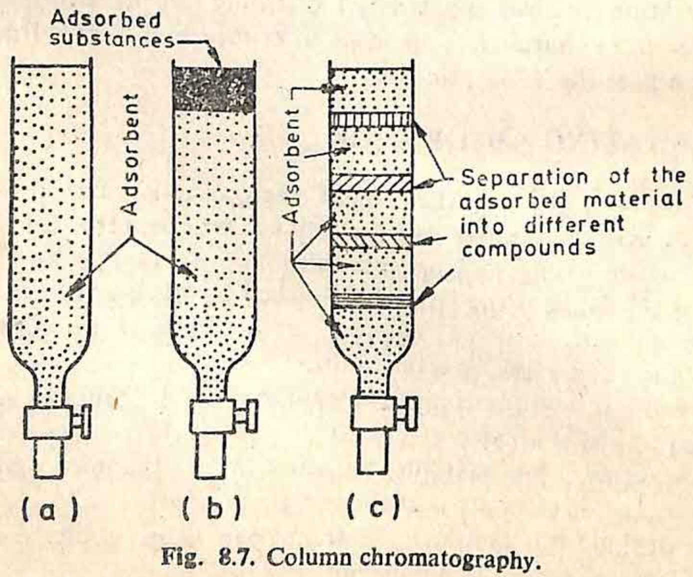

Adsorbed substances
Adsorbent
Adsorbent
Separation of the adsorbed material into different compounds
(a)
(b)
(c)

Fig. 8.7. Column chromatography.

(ii) Adsorption by charcoal cooled in liquid air helps in creating a high vacuum in a vessel which has already been evacuated by a vacuum pump.

(iii) Adsorption of toxic gases by activated charcoal makes it useful in gas masks.

(iv) Alumina and silica gels are used as adsorbents for removing moisture and for controlling humidities in rooms.

(v) Animal charcoal is used as decolorizer in the manufacture of cane sugar.

(vi) Adsorption also plays a significant role in heterogeneous catalysis.

8.6. ROLE OF ADSORPTION IN CATALYTIC REACTIONS

Many gaseous reactions proceed rapidly in the presence of suitable solid catalysts. Granular forms of catalysts are more useful due to their larger surfaces. Catalytic activity is explained due to adsorption of the reactants on the surface of the catalyst. Adsorption helps the catalytic reactions in the following ways:

(i) After the reactant molecules are adsorbed, the attack by other molecules on it becomes easier. This is because the adsorbed substance is not free to move about and escape the collision of other molecules.

(ii) Adsorbed molecules may explore their own attackable parts for reaction with other molecules.

(iii) Adsorbed molecules may get dissociated into active atoms or free radicals which are capable of reacting much faster than molecules. For example, hydrogen molecules split up into atoms during adsorption on the surface of nickel or platinum catalyst.

(iv) Due to adsorption, the concentrations of the reactants increase and hence the reactions proceed rapidly.

(v) Adsorption, particularly chemisorption, is accompanied by heat of adsorption. This provides activation energy to the reactions.

8.7. COLLOIDAL STATE

Thomas Grahm studied the process of diffusion of dissolved substances through a parchment paper on an animal membrane. He divided substances into two distinct classes as *crystalloids* and *colloids*. Substances like salt, sugar and urea, which readily passed through the membrane while in the dissolved state were called crystalloids. On the other hand, substances like glue, gelatin, albumin, starch, etc., which in the dissolved state either do not pass or diffuse very slowly through the membrane were called colloids. This arbitrary and rigid division of substances was soon proved to be incorrect because a crystalloid could behave as a colloid under different conditions and vice versa. For example, common salt, a typical crystalloid in an aqueous solution, behaves as a colloid in the benzene medium. Soap, which is a typical colloid in water, behaves as a crystalloid in alcohol. Colloids, therefore, do not represent a separate class of substances. We can speak of the *colloidal state* of matter into which every substance can be obtained by suitable methods.

8.8. TRUE SOLUTION, COLLOID AND SUSPENSION

When a substance like sugar or sodium chloride is dissolved in water, it forms a homogeneous mixture known as *true solution.* In the solution are present molecules of sugar or sodium ions and chloride ions from sodium chloride. The solute particles are invisible, do not settle down on standing and pass through a filter paper, parchment paper or an animal membrane. On the other hand, if sand is dispersed in water, the sand particles do not dissolve and settle down on standing. The particles are also large enough to be visible and do not pass through a filter paper or a parchment paper. Such a dispersion is called *suspension.*

Between these two extremes of true solutions and suspensions, there are certain mixtures in which the dispersed particles are much bigger than the molecules or ions of a true solution but smaller than the particles in a suspension. Mixtures of this intermediate particle size are called *colloids* or *sols*. Colloidal solutions are, thus, intermediate between true solutions and suspensions. The diameters of colloidal particles may range between 1 and 100 nm. The particles in the colloidal state do not settle down on standing, are not visible and can pass through a filter paper but not through parchment paper or animal membrane.

8.9. CLASSIFICATION OF COLLOIDAL SOLUTIONS (SOLS)

A colloidal solution is heterogeneous and two-phase system. One phase consists of dispersed particles of colloidal range and is called *dispersed phase.* The other phase consisting of the medium in which the colloidal particles are dispersed is called *dispersion medium.* Either of these can be a solid, liquid or gas. Thus different types of colloidal solutions (usually called sols) are possible depending upon the physical state of the two phases (Table 8.2). The gas-gas mixtures cannot form sols because of their property of diffusion to give homogeneous mixture.

TABLE 8.2 : Types of Colloidal Systems

Dispersed phase	*Dispersion medium*	*Colloidal system*	*Examples*
Solid	Solid	Solid sol	Coloured gems and glasses, some alloys, minerals
Solid	Liquid	Sol	Starch or proteins in water, paints, gold sol
Solid	Gas	Solid aerosol	Smoke, dust-storm
Liquid	Solid	Gel	Jellies, cheese, butter, boot polish
Liquid	Liquid	Emulsion	Emulsified oils, milk, cod liver oil, medicines
Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide sprays
Gas	Solid	Solid foam	Styrene foam, rubber, occluded gases
Gas	Liquid	Foam or froth	Whipped cream, lemonade froth, soap suds

Sometimes the sols are classified based on the nature of the dispersion medium like *hydrosols* or *aquasols* (in dispersion medium water), *alcosols* (in alcohol), benzosols (in benzene), aerosols (in air), etc.

Colloidal systems may also be classified as *lyophobic* (solvent-hating) and *lyophilic* (solvent-loving) sols. Lyophobic sols are those in which, if the dispersed phase is once precipitated, the sols cannot be obtained again by addition of the dispersion medium. Thus, a silver sol in water once precipitated cannot be reverted to colloidal state merely on adding water. Sols of metals, metal hydroxides and metal sulphides are other examples of lyophobic sols. They are irreversible. In case water is the dispersion medium these are known as *hydrophobic sols*. In lyophilic sols, the dispersed phase is not easily precipitated and the sols are much more stable. After precipitation, they can be easily reverted to the colloidal state on adding the dispersion medium. Gelatin, gum, starch and proteins in water are some examples of this type. Lyophilic sols are also called reversible sols. If water is the dispersion medium, they are called *hydrophilic sols*. Table 8.3 lists some distinguishing features of the two types of sols.

TABLE 8.3 : Distinction between Lyophobic and Lyophilic Sols

Lyophobic sol	*Lyophilic sol*
1. Irreversible.	Reversible.
2. Less stable and gets coagulated (precipitated) by adding electrolytes, heating or agitation.	Quite stable and not easily coagulated.
3. Prepared by indirect methods which are not so easy.	Prepared by simple solution methods.
4. Obtained from inorganic materials like metals, metal hydroxides, etc.	Obtained from organic materials such as starch, gum, gelatin, etc.
5. Carries charge.	Does not carry charge.
6. The particles are not hydrated to an appreciable extent.	The particles are hydrated appreciably.

8.10. MULTIMOLECULAR, MACROMOLECULAR AND ASSOCIATED COLLOIDS

The *multimolecular* colloidal particles consist of aggregate of atoms or small particles with diameters less than 1 nm. For example, a sol of gold contains particles of various sizes having several atoms. A sol of sulphur consists of particles having a thousand or so of S_8 molecules. These particles are held together by van der Waals forces.

The *macromolecular* colloidal particles are themselves large molecules. They have very high molecular weights varying from thousands to millions. These substances are generally polymers. Naturally occurring macromolecules are such as starch, cellulose and proteins. Artificial macromolecules are such as polyethylene, nylon, polystyrene, dacron, synthetic rubber, plastics, etc. Their molecules have big sizes and are made up of large number of atoms. The sizes of these molecules are comparable to those of colloidal particles and, therefore, their dispersions are known as macromolecular colloids. Their dispersions also resemble true solutions in some respects.

The *associated colloids* are those which behave as normal electrolytes at low concentrations but as colloids at higher concentrations. This is because at higher concentrations, they form aggregated (associated) particles called *micelles*. Soaps and synthetic detergents are examples of associated colloids. They furnish ions which may have colloidal dimensions.

$$\underset{\text{Sodium stearate (soap)}}{\mathrm{RCOONa}} \rightleftharpoons \mathrm{RCOO^-} + \mathrm{Na^+}$$

(where $R = C_{17}H_{35}$)

The long chain $RCOO^-$ ions associate at higher concentrations and form micelles. The micelles may contain 100 or more molecules.

8.11. PREPARATION OF COLLOIDAL SOLUTIONS

Colloidal solutions of lyophilic or reversible colloids can be prepared by simple treatment with the dispersion medium. Starch, gum arabic, gelatin or egg albumin forms its colloidal solution by merely dissolving it in water.

Lyophobic or irreversible sols are prepared by two types of methods called *dispersion methods* and *condensation methods*.

Dispersion Methods

In these methods, the coarse particles are broken to the particles of colloidal size. This may be achieved in the following ways:

MECHANICAL DISPERSION

The coarse suspension of the substance (to be dispersed) is brought into a colloidal state in the dispersion medium by grinding it in a colloid mill (Fig. 8.8), ball mill or ultrasonic disintegrator. The colloid mill consists of two metal discs, close together, rotating at high speed in the opposite directions when the suspension particles are torn off to the colloidal dimensions.

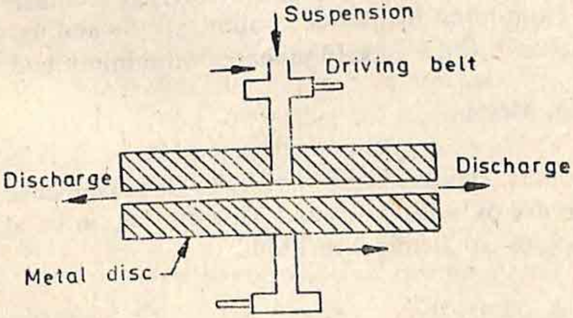


Fig. 8.8 Colloid mill.

ELECTRICAL DISPERSION OR BREDIG'S ARC METHOD

Colloidal metal sols of gold, silver, platinum, etc., are prepared by this method. An electric arc is struck under the dispersion medium (commonly cold water) between electrodes of the metal to be dispersed (Fig. 8.9). The intense heat of the arc converts the metal into vapours which are condensed by the ice-cold water. A little alkali (sodium hydroxide or potassium carbonate) is added which stabilizes the sol.

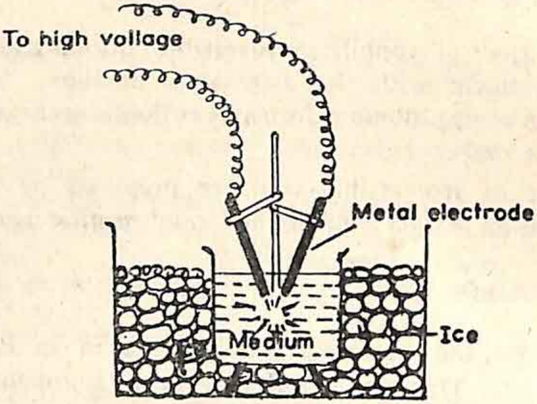


Fig. 8.9 Bredig's arc method.

PEPTIZATION

Peptization is the process by which certain substances are converted to the colloidal state when shaken with water containing very small amount of an electrolyte, which acts as the *peptizing agent*. For example, a reddish-brown positively charged sol is obtained when freshly precipitated ferric hydroxide is shaken with water containing a small quantity of ferric chloride electrolyte. Similarly, colloidal solution of aluminium hydroxide is obtained by adding very dilute hydrochloric acid to the freshly prepared aluminium hydroxide.

Condensation Methods

In these methods, small ions or molecules are condensed together to form particles of colloidal size. This may again be achieved by physical methods or chemical methods.

(i) PHYSICAL METHODS

Some examples of such methods are:

Excessive cooling The colloidal solution of ice in an organic solvent like ether or chloroform is obtained by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal dimension.

Exchange of solvent Colloidal solution of a substance which is soluble in alcohol but practically insoluble in water (*e.g.*, phosphorus, sulphur, etc.) can be obtained by pouring a small amount of its alcoholic solution in excess of water. A milky colloidal solution of phenolphthalein indicator results when its alcoholic solution is poured into water.

Passing vapours of an element into a liquid When vapours of sulphur or mercury are passed into water containing a little stabilizing agent like ammonium citrate, the colloidal solution is formed.

(ii) CHEMICAL METHODS

Sols can be prepared by chemical reactions involving oxidation, reduction, hydrolysis and double decomposition.

Oxidation A colloidal solution of sulphur can be obtained by bubbling H_2S through an aqueous solution of sulphur dioxide or some other oxidizing agent such as bromine water, nitric acid, etc. Colloidal selenium can also be obtained by oxidation of H_2Se.

$$SO_2+2H_2S \longrightarrow 2H_2O+\underset{\text{(Sol)}}{3S}$$

$$H_2S+Br_2 \longrightarrow 2HBr+\underset{\text{(Sol)}}{S}$$

The colloidal solution thus obtained is purified by dialysis.

Reduction Sols of metals like silver, gold, platinum, etc., can be obtained by treating their solutions with a suitable reducing agent such as stannous chloride, formaldehyde or hydrazine.

$$2AuCl_3+3SnCl_2 \longrightarrow 3SnCl_4+\underset{\text{(Sol)}}{2Au}$$

Hydrolysis Sols of hydrated oxides of weakly electropositive metals like iron, aluminium, tin, etc., can be obtained by hydrolysis. For example, colloidal ferric hydroxide is prepared by boiling a dilute solution of ferric chloride when hydrolysis occurs.

$$FeCl_3+3H_2O \longrightarrow 3HCl+\underset{\text{(Sol)}}{Fe(OH)_3}$$

Double decomposition Arsenious sulphide sol can be prepared by passing H_2S through a dilute solution of arsenious oxide in water when double decomposition takes place.

$$As_2O_3+3H_2S \longrightarrow 3H_2O+\underset{\text{(Sol)}}{As_2S_3}$$

Silver halide sol can also be obtained by mixing a dilute solution of silver salt with an alkali halide in equivalent amount.

8.12. PURIFICATION OF COLLOIDAL SOLUTIONS

Colloids obtained by various methods are impure and contain impurities of electrolytes and other soluble substances. These impurities may destabilize the sol. Hence they require to be purified. A very important method of removal of soluble impurities is known as dialysis.

Dialysis

Particles of true solutions (made up of ions and molecules) can pass through parchment paper or cellophane membrane. On the other hand, sol particles cannot pass through these membranes. A bag made up of such a membrane is filled with the colloidal solution and is then suspended in fresh water Warm water may be used to hasten the dialysis (Fig. 8.10, *a*). Movement of ions across the membrane can be expedited by applying electric current through two electrodes. This method is very fast and is known as *electrodialysis* (Fig. 8.10, *b*).

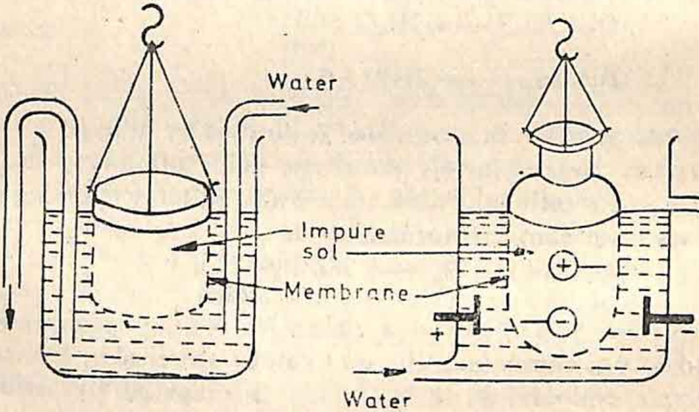


Fig 8.10. (*a*) Dialysis. (*b*) Electrodialysis.

Ultrafiltration

It is a process similar to filtration, except that a membrane is used which permits the passage of electrolyte and dispersion medium and not the colloid. For this purpose, ordinary filter paper impregnated with colloid ions (called *ultrafilter*) is used. Other filter media are sintered glass and unglazed porcelain. By this process, it is possible to separate in the form of a slime, colloid particles from media containing electrolytes. These slimes can be suspended again in pure media to obtain pure colloidal solution.

8.13. PROPERTIES OF COLLOIDAL SOLUTIONS

Heterogeneous Nature

Colloidal solutions are heterogeneous in nature and consist of two phases, the *dispersed phase* and the *dispersion medium.*

Filtrability

Colloidal particles are smaller in size than the size of the pores of the ordinary filter paper, therefore, they pass through them. However, the particles cannot pass through parchment paper, animal membrane or ultrafilter.

Osmotic Pressure

Colloidal particles have very low osmotic pressure because of poor interactions with the medium. Lyophilic systems have relatively higher osmotic pressure as compared to that of lyophobic systems. The average molecular masses of colloidal particles can be determined making use of the osmotic pressure measurements.

Brownian Movement

Robert Brown, a botanist discovered in 1827 that pollen grains placed in water do not remain at rest but move about ceaselessly. Later on, this phenomenon was observed in case of colloidal particles when they were seen under an ultramicroscope. The particles were found to be in constant motion in zag-zag path in all possible directions (Fig. 8.11). This erratic motion of the colloidal particles is called Brownian movement. It is due to the collisions of the colloidal particles with the molecules of the dispersion medium.

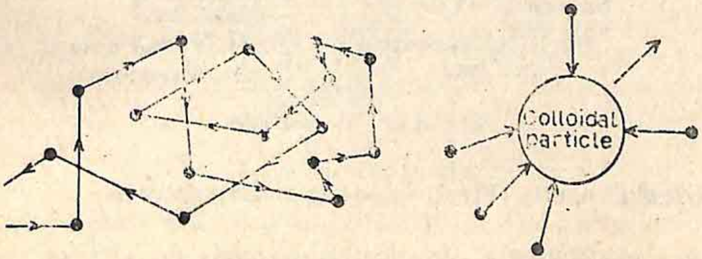


Fig 8.11. Brownian movement.

Diffusion

Colloidal particles, like solute particles, diffuse from a region of higher concentration to that of lower concentration. The slower movement of colloidal particles gives rise to slower rate of diffusion. The process can be used to separate colloids from colloids of different sizes and also to find out their sizes.

Sedimentation

Under the influence of gravity, the sol particles tend to settle down very slowly. This rate of settling down or sedimentation can be accelerated by the use of a high speed centrifuge called *ultracentrifuge*.

Optical Property (Tyndall Effect)

Tyndall, in 1869, observed that when a strong converging beam of light is passed through a colloidal solution placed in a dark place, the path of the beam gets illuminated by a bluish light. This phenomenon is called *Tyndall effect* and the illuminated path is known as *Tyndall cone* (Fig. 8.12). The effect is due to the scattering of light by the colloidal particles. The dust particles become visible in a semi-darkened room when a sun beam enters or light is thrown from a projector. This is a familiar example of the Tyndall effect. The dust particles are large enough to scatter light and hence the path becomes visible.

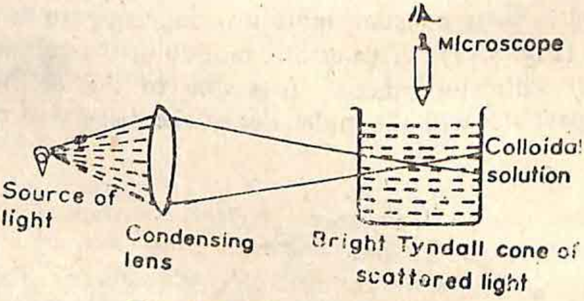
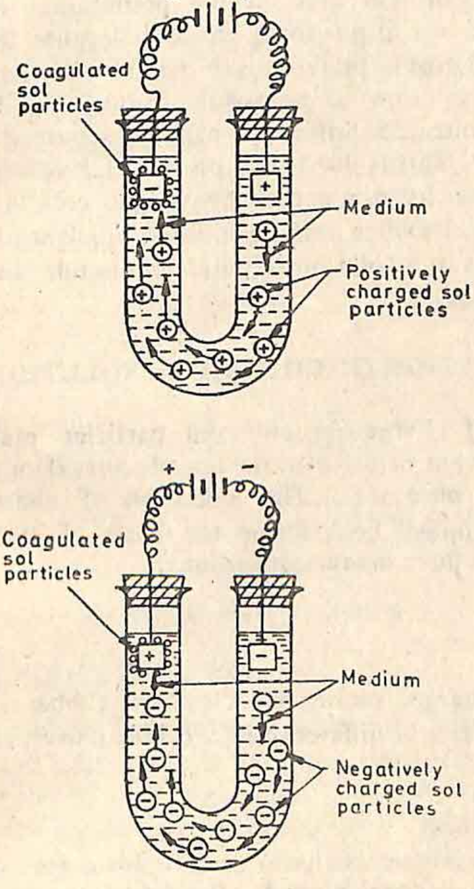


Fig. 8.12. Tyndall effect.

Electrical Property (Electrophoresis or Cataphoresis)

Colloidal particles are electrically charged—positive or negative. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles. This is why a sol is stable and particles do settle down. Silver, gold, platinum and arsenious sulphide particles in their respective sols are negatively charged while particles of aluminium hydroxide and ferric hydroxide are positively charged. The existence of the electric charge is shown by the phenomenon of electrophoresis or cataphoresis (Fig. 8.13). It involves the motion of colloidal particles either towards the cathode or anode, under the influence of an electric field. The colloidal solution is placed in a U-tube fitted with platinum electrodes. On passing an electric current, the charged colloidal particles move towards the oppositely charged electrode.



Coagulated sol particles
Medium
Positively charged sol particles
Coagulated sol particles
Medium
Negatively charged sol particles

Fig. 8.13. Demonstration of electrophoresis.

Diffusion

Colloidal particles, like solute particles, diffuse from a region of higher concentration to that of lower concentration. The slower movement of colloidal particles gives rise to slower rate of diffusion. The process can be used to separate colloids from colloids of different sizes and also to find out their sizes.

Sedimentation

Under the influence of gravity, the sol particles tend to settle down very slowly. This rate of settling down or sedimentation can be accelerated by the use of a high speed centrifuge called *ultracentrifuge*.

Optical Property (Tyndall Effect)

Tyndall, in 1869, observed that when a strong converging beam of light is passed through a colloidal solution placed in a dark place, the path of the beam gets illuminated by a bluish light. This phenomenon is called *Tyndall effect* and the illuminated path is known as ***Tyndall cone*** (Fig. 8.12). The effect is due to the scattering of light by the colloidal particles. The dust particles become visible in a semi-darkened room when a sun beam enters or light is thrown from a projector. This is a familiar example of the Tyndall effect. The dust particles are large enough to scatter light and hence the path becomes visible.

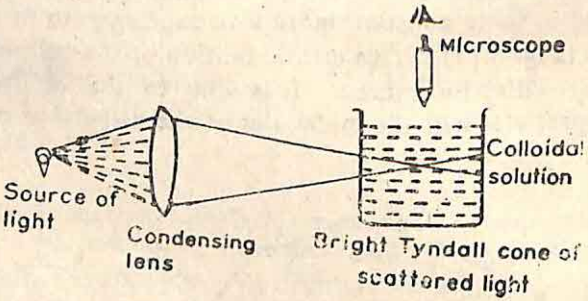


Fig. 8.12. Tyndall effect.

Electrical Property (Electrophoresis or Cataphoresis)

Colloidal particles are electrically charged—positive or negative. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles. This is why a sol is stable and particles do settle down. Silver, gold, platinum and arsenious sulphide particles in their respective sols are negatively charged while particles of aluminium hydroxide and ferric hydroxide are positively charged. The existence of the electric charge is shown by the phenomenon of electrophoresis or cataphoresis (Fig. 8.13). It involves the motion of colloidal particles either towards the cathode or anode, under the influence of an electric field. The colloidal solution is placed in a U-tube fitted with platinum electrodes. On passing an electric current, the charged colloidal particles move towards the oppositely charged electrode.

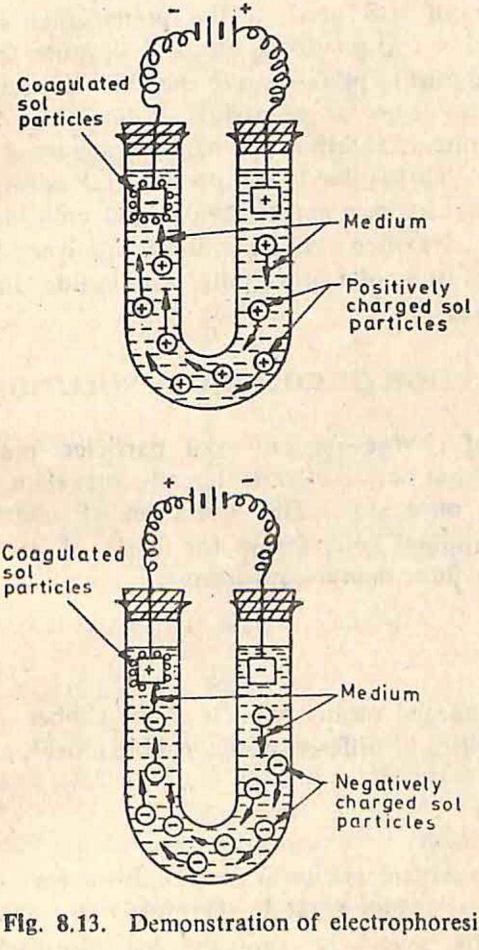

-
+
Coagulated sol particles
Medium
Positively charged sol particles
+
-
Coagulated sol particles
Medium
Negatively charged sol particles

Fig. 8.13. Demonstration of electrophoresis.

8.14. ORIGIN OF CHARGE ON COLLOIDS

The origin of charge on the sol particles has been ascribed to the *preferential adsorption* of a certain type of ions present in the dispersion medium. The negative charge on the metal sols prepared by the Bredig's arc method is due to the adsorption of hydroxyl ions furnished by the traces of alkali added to produce a stable sol.

When two or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. Thus, negative charge on arsenious sulphide sol is due to the preferential adsorption of sulphide ions produced by the ionization of H_2S used in the preparation of the sol. A ferric hydroxide sol is positively charged because the sol particles adsorb the ferric ions in preference to the chloride ions.

If a dilute solution of potassium iodide is added to a slight excess of silver nitrate solution, a positively charged sol of silver iodide is formed. This is due to the preferential adsorption of silver ions. On the other hand, a negatively charged colloidal solution of silver iodide results when a dilute solution of silver nitrate is added to a slight excess of a solution of potassium iodide due to adsorption of iodide ions.

8.15. COAGULATION OF COLLOIDAL SOLUTIONS

The presence of charge on colloidal particles makes colloidal solutions somewhat better electrical conductors than the dispersion medium in the pure state. The migration of charged colloidal particles in an applied field forms the basis of electrodeposition of colloids. This finds many applications:

Rubber Plating

The negatively charged rubber particles from rubber sol are deposited on wires, handles of different tools, rubber gloves, etc.

Sewage Disposal

Sewage water contains particles of dirt, rubbish, etc., which are of colloidal size, carry charge and, therefore, do not settle down easily. The particles can be removed by electrophoresis. Dirty water is passed through a tunnel fitted metallic electrodes which are maintained at high potential difference. The particles migrate to the oppositely charged electrodes, lose their charges and are coagulated. The deposited matter is used as a manure and the water left behind, is used for irrigation.

Cottrell Precipitator

Smoke is made free of colloidal particles by passing it through Cottrell precipitator (Fig 8.14) installed in the chimney of an industrial plant. The precipitator consists of two metal discs maintained at a high potential difference. The smoke or dust particles get deposited and finally precipitated down while free gases escape from the chimney.

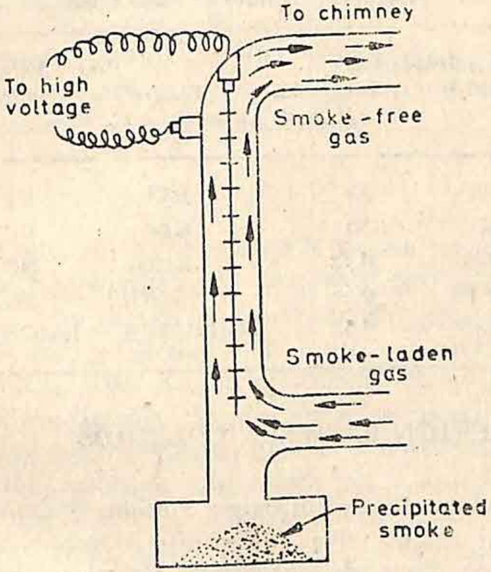


Fig. 8.14 Cottrell precipitator.

8.16. HARDY-SCHULZE RULE

When an electrolyte is added to a colloidal solution, it furnishes both positive and negative ions. The sol particles take up ions which are charged opposite and thus they get neutralized. The neutral particles then unite with one another to form bigger particles or the sol gets coagulated or flocculated. Thus coagulation is the process of conversion of particles of a colloidal solution into large-sized particles which ultimately settle down as a precipitate. Hardy and Schulze observed that the coagulating power of an electrolyte depends upon the valence of ion carrying opposite charge to that of the dispersed phase. Thus for the coagulation of sols carrying negative charge (like arsenious sulphide sol), Al^{3+} ions are more effective than Ba^{2+} or Na^+ ions. Similarly, for the coagulation of sols carrying positive charge (like ferric hydroxide sol), PO_4^{3-} ions are more effective than SO_4^{2-} or Cl^- ions.

The minimum concentration of an electrolyte required to cause coagulation or flocculation of a sol is called its ***coagulation*** or ***flocculation value*** and is usually expressed in millimoles per litre of the mixed solution. Flocculation values of some common electrolytes for negatively charged arsenious sulphide sol and positively charged ferric hydroxide sol are given in Table 8.4.

TABLE 8.4 : Flocculation Values of Some Common Electrolytes

Arsenious sulphide sol			*Ferric hydroxide sol*		
Electrolyte	*Cation*	*Flocculation value*	*Electrolyte*	*Anion*	*Flocculation value*
NaCl	Na^+	50	KCl	Cl^-	132
KCl	K^+	50	KBr	Br^-	132
$MgCl_2$	Mg^{2+}	0.72	KNO_3	NO_3^-	132
$BaCl_2$	Ba^{2+}	0.69	K_2SO_4	SO_4^{2-}	0.21
$AlCl_3$	Al^{3+}	0.95	$K_3[Fe(CN)_6]$	$[Fe(CN)_6]^{3-}$	0.096

8.17. INTERACTION BETWEEN COLLOIDS

Certain lyophobic colloids can cause mutual coagulation on being mixed together mainly due to neutralization of electrical charges of opposite types. Thus when negatively charged arsenious sulphide sol is mixed with positively charged ferric hydroxide sol in suitable proportions, coagulation of both sols takes place simultaneously.

Certain lyophilic sols can protect the lyophobic sols from coagulation by electrolytes. This is due to the adsorption of lyophilic sol particles by lyophobic sol particles. Thus, a gold sol is protected by gelatin, gum or starch. Zsigmondy introduced the term *gold number* to measure the protective power of different colloids. It is defined as the minimum number of milligrams of the dry protective colloid which will check the coagulation of 10 ml of a standard red gold sol (i. e., prevent its colour becoming blue) on adding 1 ml of a 10% sodium chloride solution. Obviously, the smaller the gold number of a lyophilic colloid, the greater is its protective power.

8.18. EMULSIONS

Liquid-liquid sols are known as *emulsions*. They are of two types:

Oil-in-Water Emulsions

In these, oil forms the dispersed phase while water is the dispersion medium. Common examples of such emulsions are milk (fat globules dispersed in water) and vanishing cream.

Water-in-Oil Emulsions

In such emulsions, water is the dispersed phase and oil forms the dispersion medium. Butter and cold cream are the common examples of this type of emulsions.

Emulsification

The process of making an emulsion is known as *emulsification*. Emulsions may be obtained by vigorously agitating a mixture of both the liquids. But this gives an unstable emulsion. The dispersed droplets come together and form a separate layer. To stabilize an emulsion, the addition of a small quantity of a third substance called *emulsifying agent* or *emulsifier* is essential. Soaps and detergents are most frequently used as emulsifiers. They coat the drops of the emulsion and check the coming together of droplets. Washing action of soaps and detergents is due to the emulsification of grease and taking it away in the water along with dirt and dust present on grease. A wide variety of pharmaceutical preparations are emulsions, e. g., emulsions of cod liver oil and halibut liver oil. These emulsified oils are easily acted upon by the digestive juices in the stomach and hence are readily digested. The disinfectants such as phenyl, detol, etc., give emulsions of the oil-in-water type when poured into water. Emulsions play an important role in industry. The froth flotation process used for concentrating metal sulphide minerals involves the treatment of the pulverized ore in an oil emulsion.

Emulsions can be broken down (*demulsification*) to give back the liquids by physical methods such as freezing, boiling, filtration etc., and by chemical methods which destroy the emulsifiers. A common example of demulsification is the separation of cream from milk by centrifugation.

EXERCISES

8.1 Define the terms adsorption and absorption with appropriate examples.
8.2 What type of binding forces are present in adsorption ?
8.3 Explain the following :
 (i) Adsorbent (ii) Adsorbate (iii) Desorption
 (iv) Positive adsorption (v) Negative adsorption
8.4 Distinguish between physical adsorption and chemisorption.
8.5 Enumerate the factors on which the amount of a gas adsorbed on the surface of a solid depend.
8.6 Discuss the effect of 'nature of gas and nature of adsorbent' on adsorption.
8.7 Describe how temperature and pressure affect adsorption.
8.8 (i) What are adsorption isotherms ?
 (ii) Give Freundlich equation for adsorption of gases.
8.9 What is meant by activation of a surface ? How is it brought about ?
8.10 Discuss the adsorption of solute from solution and write the Freundlich isotherm.
8.11 Give the applications of adsorption.
8.12 What role does adsorption play in catalytic reactions ?
8.13 What is meant by the colloidal state of matter ?
8.14 How will you distinguish among true solutions, colloidal solutions and suspensions ?
8.15 (i) What is the size of sol particles ?
 (ii) What are various types of sols ? Give examples.
8.16 Give the distinction between lyophilic and lyophobic sols.
8.17 What are multimolecular and macromolecular colloids ? Give examples.
8.18 Describe briefly the different methods employed in the preparation of colloidal solutions.
8.19 Describe the properties of colloids with special reference to optical and electrical properties.
8.20 Write short notes on :
 (i) Brownian movement (ii) Cataphoresis
 (iii) Tyndall effect (iv) Protective action of sols.
8.21 Explain what happens when:
 (i) A beam of light is passed through a colloidal solution.
 (ii) An electrolyte is added to a colloidal solution.
 (iii) An electric current is passed through a colloidal solution.
 (iv) A lyophilic sol is mixed with a lyophobic sol.
8.22 Explain the following:
 (i) Hardy-Schulze rule
 (ii) Gold number.
8.23 What are emulsions ? How are they classified ?
8.24 What are emulsifiers ? What role do they play in forming emulsions ?
8.25 Give some applications of emulsions.
8.26 Explain the following:
 (i) Flocculation
 (ii) Demulsification
 (iii) Peptization
 (iv) Sedimentation
 (v) Origin of charge on colloidal solution.

Unit 9

The Oxygen Family

Electronic structure and trends in properties. Ozone: structure, preparation, properties and uses. Industrial preparation of sulphuric acid. Preparation, properties and uses of sodium sulphite and metabisulphite.

In class XI we have studied the elements belonging to groups IA to VA of the Periodic Table. In this Unit, we will study the elements of group VIA, the oxygen family. This group consists of five elements—oxygen, sulphur, selenium, tellurium and polonium. Oxygen is the most abundant element in the earth's crust (46.6%). It also occurs free and is about 21% by volume of the atmosphere. Sulphur occurs to the extent of 0.52% in the earth's crust (Table 9.1). These elements are collectively known as *chalcogens*, i.e., ore forming elements because most metals occur as oxides or sulphides.

9.1. GENERAL TRENDS

The elements of the oxygen family have the electronic configuration ns^2np^4 (Table 9.1) and tend to attain the noble gas configuration by gaining two electrons or by sharing two electrons.

The elements show a general gradation in their properties. Oxygen and sulphur are typical non-metals, selenium and tellurium are semiconductors while polonium is metallic in character. As we move down the group, there is a general increase in the atomic and ionic radii (Fig. 9.1), densities (Fig. 9.2) and melting and boiling points (Fig. 9.3) of the elements. The ionization energies and electronegativities of the elements are high and they decrease as we

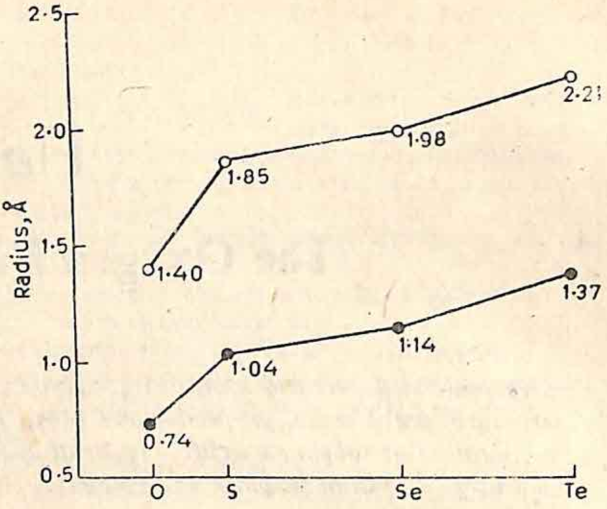


Fig. 9.1. Atomic (●) and ionic (O) radii of the elements of oxygen family.

TABLE 9.1: Some Properties of the Elements of Oxygen Family

Element	*Atomic number*	*Electronic configuration*	*Oxidation state*	*Abundance in earth's crust, ppm*
O	8 [He]	$2s^22p^4$	-2	466 000
S	16 [Ne]	$3s^23p^4$	$-2, +2, +4, +6$	520
Se	34 [Ar]	$3d^{10}4s^24p^4$	$-2, +2, +4, +6$	0.09
Te	52 [Kr]	$4d^{10}5s^25p^4$	$-2, +2, +4, +6$	0.002
Po	84 [Xe]	$4f^{14}5d^{10}6s^26p^4$	$+2, +4$	Trace

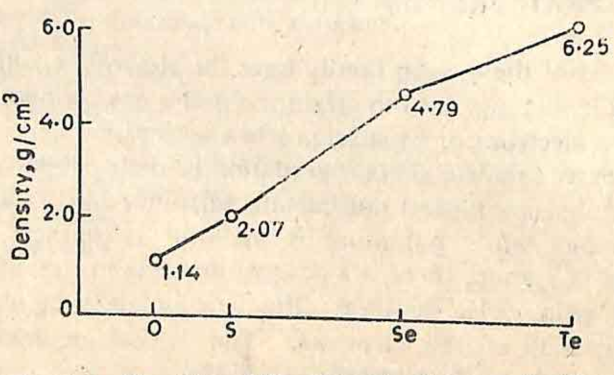


Fig. 9.2. Densities of the elements of oxygen family.

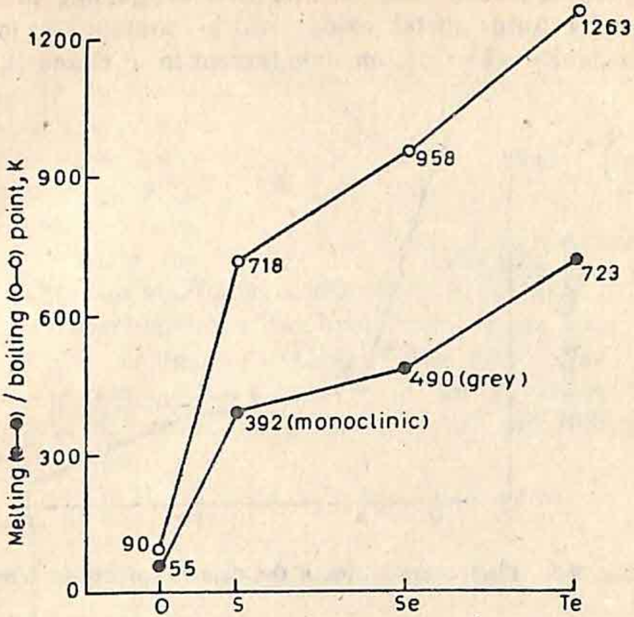


Fig. 9.3. Melting and boiling points of the elements of oxygen family.

go down the group (Figs. 9.4 and 9.5).

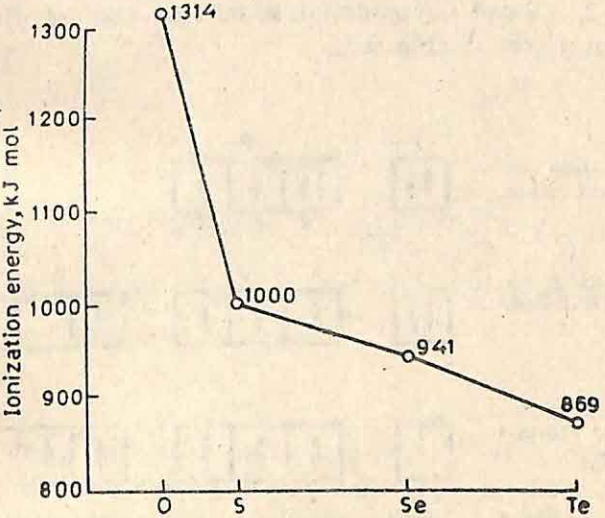


Fig. 9.4. Ionization energies of the elements of oxygen family.

The high electronegativity of oxygen (second only to fluorine) suggests that it tends to complete its octet by gaining two electrons and thereby forms metal oxides which contain O^{2-} ions. Thus oxygen exhibits −2 oxidation state (except in F_2O and H_2O_2). The electronegativities of the other elements of the group are comparatively low and they show much less tendency to be in −2 oxidation state. The last element polonium does not exhibit negative oxidation state at all (Table 9.1). Except oxygen, the other elements show +2, +4 and +6 oxidation states also because of the presence of vacant *d* orbitals (Fig. 9.6).

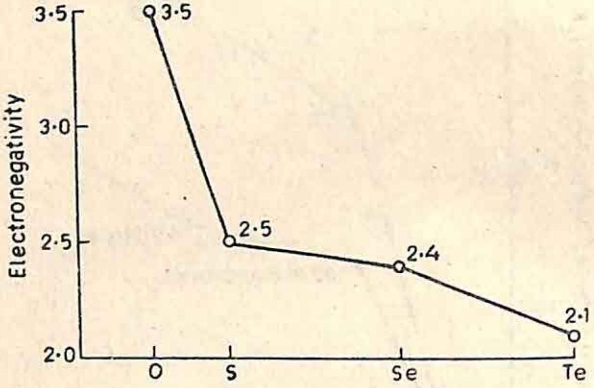


Fig. 9.5. Electronegativities of the elements of oxygen family.

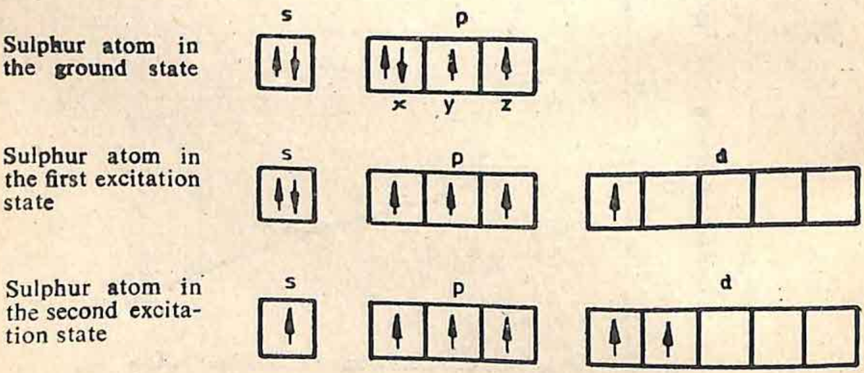

Sulphur atom in the ground state
s
p
x
y
z
Sulphur atom in the first excitation state
s
p
d
Sulphur atom in the second excitation state
s
p
d

Fig. 9.6. Various oxidation states shown by sulphur.

Because of its small size, high electronegativity and non-availability of *d* orbitals, oxygen shows anomalous behaviour. It is a

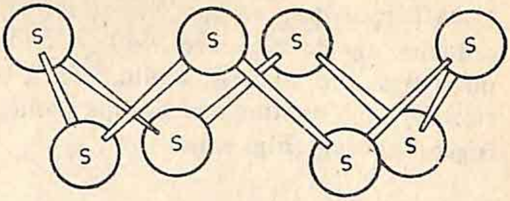


Fig. 9.7. Puckered ring structure of S_8 molecules.

gas and exists as diatomic molecules. The other elements are solids and exist as S_8 and Se_8 molecules at room temperature and have a puckered ring structure (Fig. 9.7). Oxygen shows —2 oxidation state while the other elements show additional oxidation states (Table 9.1). Melting and boiling points (Fig. 9.8) of the hydride of oxygen (*i.e.*, water) are much higher compared to those of the hydrides of the other elements of the group. This is because of the hydrogen bonding in water which, in turn, is due to the small size and high electronegativity of oxygen.

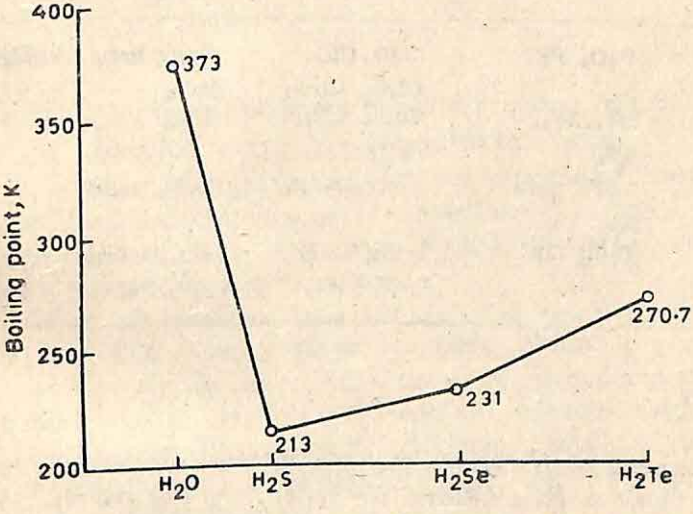


Fig. 9.8. Boiling points of hydrides of the elements of oxygen family.

9.2. COMPOUNDS

Hydrides

The elements of this family form volatile hydrides of the type H_2R (where R=O, S, Se, Te or Po). The stability of the hydrides decreases from H_2O to H_2Po. H_2S, H_2Se and H_2Te are prepared by the action of acid on metal sulphides, selenides and tellurides. For example:

$$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$$

All hydrides, except water, are offensive smelling gases, act as reducing agents and are weakly acidic. Water is a colourless, odourless and neutral liquid. As it has been said earlier, exceptionally high melting and boiling points of water are due to hydrogen bonding (Fig. 9.8).

Halides

The elements of the oxygen family form a large number of halides (Table 9.2). Sulphur, selenium and tellurium show a maximum covalency of six in their fluorides which are colourless gases.

TABLE 9.2: Halides of Elements of Oxygen Family.

Element	*Fluorides*	*Chlorides*	*Bromides*	*Iodides*
O	F_2O_2, F_2O	Cl_2O, ClO_2 Cl_2O_6, Cl_2O_7	Br_2O, BrO_2 BrO_3	I_2O_4, I_4O_9 I_2O_5
S	S_2F_2, SF_4, SF_6	S_2Cl_2, SCl_2, SCl_4	S_2Br_2	——
Se	Se_2F_2, SeF_4 SeF_6	Se_2Cl_2, $SeCl_4$,	Se_2Br_2, $SeBr_4$	——
Te	TeF_4, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
PO	——	$PoCl_2$ $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

Oxides

The elements of this group, with the obvious exception of oxygen, form dioxides RO_2 (where R=S, Se, Te or Po) and also trioxides RO_3 (where R=S, Se or Te). The dioxides are obtained when the elements are burnt in air. The best known sulphur trioxide is prepared by the catalytic oxidation of sulphur dioxide.

9.3. STRUCTURE OF OXYGEN MOLECULE

The electronic structure of oxygen, $:\ddot{O}:\ :\ddot{O}:$ does not show any unpaired electron and therefore it fails to account for the paramagnetic behaviour of the molecule. It is suggested that in the structure two oxygen atoms are joined by an electron-pair bond (shown by the line bond) and two 3-electron bonds. The 3-electron bonds have one unpaired electron each and account for paramagnetism.

$$:\!O\overset{\cdots}{\underset{\cdots}{-}}O\!:$$

9.4. OZONE

Ozone is very reactive and does not remain for long in atmosphere at sea level. However, it is formed in the upper layers of atmosphere (about 20 km above the earth's surface) by the action of ultraviolet light on oxygen. The ozone layer protects the earth's surface from an excessive concentration or the harmful ultraviolet radiation.

Preparation

When cold, dry oxygen is subjected to a *silent* electric discharge in an ozonizer, about 10% oxygen gets converted into ozone.

$$3O_2 \rightleftharpoons 2O_3;\ \Delta H = +142\ \text{kJ mol}^{-1} \text{ of ozone formed.}$$

The silent electric discharge is used to avoid the decomposition of the endothermic ozone. In a sparking electric discharge, heat is produced which will decompose ozone.

Two types of ozonizers used are shown in Fig. 9.9 (Siemen's ozonizer) and Fig. 9.10 (Brodie's ozonizer). Siemen's ozonizer consists of two coaxial glass tubes sealed at one end and coated with tin foil as shown. When the coatings are connected with the terminals of a powerful induction coil, the oxygen gas passing through the annular space is subjected to silent electric discharge and becomes ozonized oxygen.

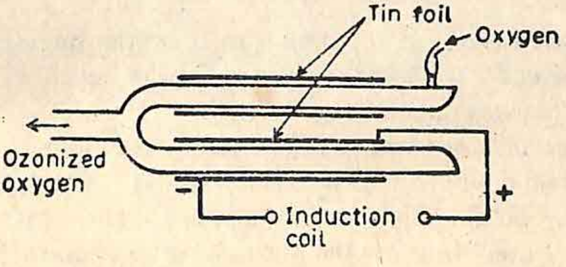


Fig. 9.9. Siemen's ozonizer.

In Brodie's ozonizer, the annular space is surrounded with dilute sulphuric acid. Copper electrodes are dipped in the acid and are connected to an induction coil. When oxygen passes through the annular space, it is subjected to silent electric discharge and gets partially changed into ozone.

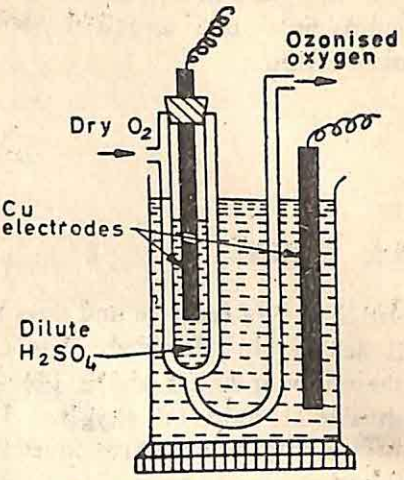


Fig. 9.10. Brodie's ozonizer.

Properties

The pale blue ozone gas can be liquified to a deep blue liquid and solidified to voilet black crystals. The gas has characteristic odour and is harmful if its concentration exceeds 100 ppm. It is an endothermic compound and is, therefore, unstable and reactive.

Ozone is a strong oxidizing agent—much more powerful than molecular oxygen. It oxidizes ferrous to ferric, lead sulphide to lead sulphate, iodide to iodine, iodine to iodic acid and potassium ferrocyanide to potassium ferricyanide.

$$2Fe^{2+}+2H^{+}+O_3 \longrightarrow 2Fe^{3+}+H_2O+O_2$$

$$PbS+4O_3 \longrightarrow PbSO_4+4O_2$$

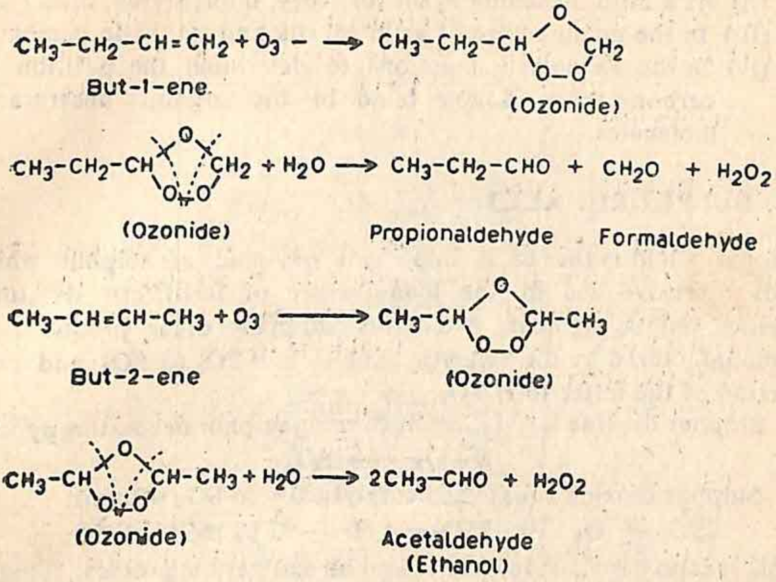
$$2I^{-}+H_2O+O_3 \longrightarrow I_2+2OH^{-}+O_2$$

$$I_2+5O_3+H_2O \longrightarrow 2HIO_3+5O_2$$

$$2K_4Fe(CN)_6+O_3+H_2O \longrightarrow 2K_3Fe(CN)_6+2KOH+O_2$$

The reaction of ozone with iodine is used for the quantitative estimation of ozone. The iodine liberated in the reaction is titrated with standard thiosulphate solution.

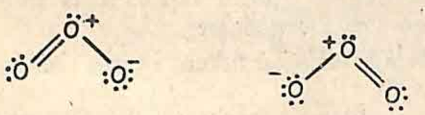
Ozone reacts with unsaturated organic compounds containing carbon-carbon double bonds to form ozonides. These products are hydrolysed to obtain aldehydes and ketones. The reaction (called *ozonolysis*) is used to locate the position of carbon-carbon double bond in the original unsaturated compound. For example:



Mercury is partially oxidized with ozone and thereby sticks to the walls of the vessel in which it is contained. This is called 'tailing' of mercury and serves as a test for the presence of ozone.

Structure

Ozone is a resonance hybrid of the following two structures:



The two oxygen-oxygen bond lengths in the molecule are identical and have the value 1.28 Å. This value is intermediate between the bond length for an oxygen-oxygen double bond and that for an oxygen-oxygen single bond. The ozone molecule is angular with a bond angle of about 117°. The scale model of ozone molecules may be represented as shown in Fig. 9.11.

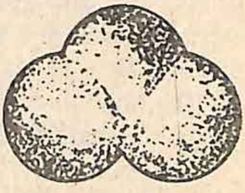


Fig. 9.11. Scale model of ozone molecule.

Uses

Ozone is used:

(i) As a germicide and disinfectant for purification of air in crowded places and for sterilizing water.

(ii) As a mild bleaching agent for ivory, flour, starch, oils, etc.

(iii) In the manufacture of artificial silk and synthetic camphor.

(iv) In the ozonolysis reactions to determine the position of carbon-carbon double bond in the organic unsaturated molecules.

9.5. SULPHURIC ACID

Sulphuric acid is the most important oxy-acid of sulphur which finds extensive use in the manufacture of fertilizers, dyestuffs, plastics, paints, pigments, explosives and many other products. It is manufactured by the catalytic oxidation of SO_2 to SO_3 and conversion of the latter to H_2SO_4.

Sulphur dioxide is obtained by burning sulphur or roasting pyrites:

$$S + O_2 \longrightarrow SO_2$$

Sulphur dioxide is oxidized catalytically to SO_3 with air:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \triangle H = -95 \text{ kJ mol}^{-1} \text{ of } SO_3$$

This reaction is slow, reversible and an exothermic process. According to the Le Chatelier's principle, low temperature, use of a catalyst, excess of air and high pressure should favour the formation of sulphur trioxide. The optimum working conditions for the reaction are found to be:

(i) Temperature: Between 675 and 725.

(ii) Catalyst: Platinum, ferric oxide or vanadium pentoxide. These days vanadium pentoxide is preferred as it is much cheaper than platinum and is not easily poisoned.

(iii) Sulphur dioxide and oxygen taken in the molecular ratio 2:3 give the optimum yield.

(iv) Though a high pressure favours the forward reaction, usually the atmospheric pressure is maintained. This saves the extra expenses and also the plant is less corroded at atmospheric pressure than at higher pressure.

The flow diagram of the *contact process* which is usually employed for the manufacture of sulphuric acid is shown in Fig. 9.12.

The gases obtained by burning sulphur or iron pyrites contain impurities like arsenious oxide, sulphur dust and acid fog which can poison the catalyst. These impurities are removed in the *precipitator*. The gases are then passed through *cooling pipes* and are washed in *scrubber* by a down-flowing stream of water. The moist gases are dried in *drying tower* by a spray of concentrated sulphuric acid coming down. The dried gases are passed through *arsenic*

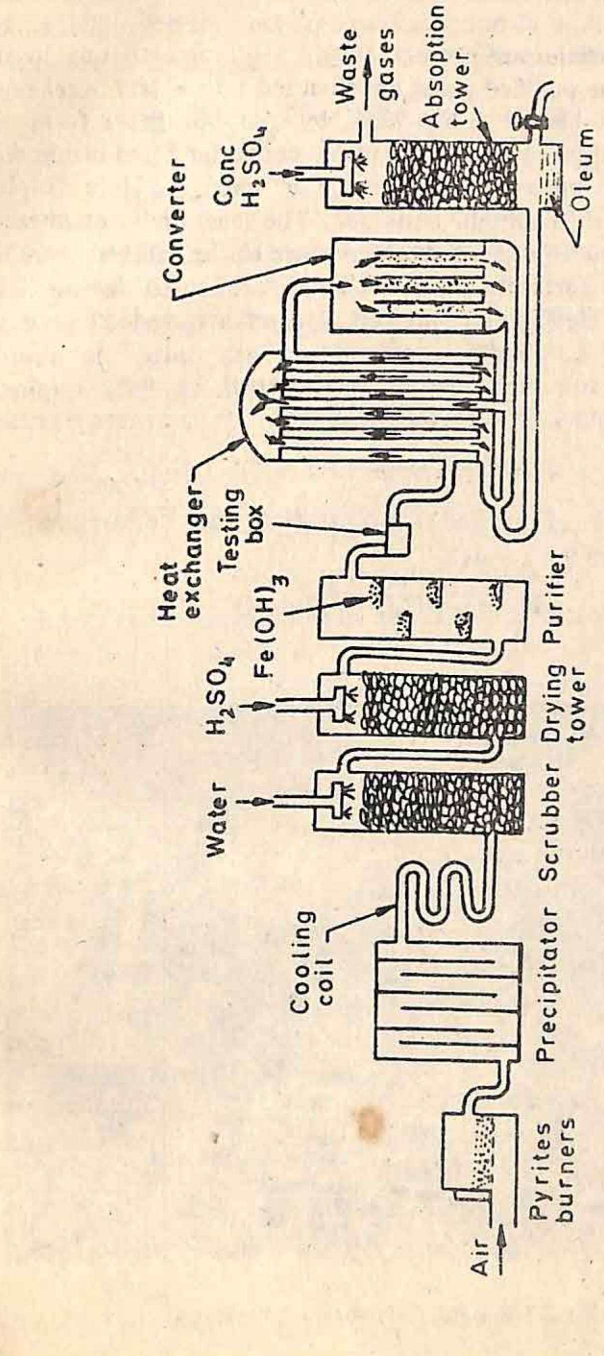


Fig. 9.12. Contact process for the manufacture of sulphuric acid.

purifier which contains shelves holding gelatinous ferric hydroxide. Arsenic oxide is absorbed by ferric hydroxide. The gases are then passed in a *testing box* to find whether they are free from impurities or not. In the box, a strong beam of light is passed against the gases. If any particles are present, they get illuminated due to the Tyndall effect. The purified gases are then led into a *heat exchanger* where they are pre-heated to 675-725K by the hot gases from the *converter*. The hot gases now enter into a converter fitted inside with iron tubes containing vanadium pentoxide catalyst. Here sulphur dioxide is oxidized to sulphur trioxide. The reaction is exothermic and the heat produced raises the temperature of the catalyst to 725K. Once the process starts, the gases need not be heated in the heat exchanger but passed directly into an *absorption tower*. The gases containing mainly sulphur trioxide and nitrogen enter the absorption tower where sulphur trioxide is absorbed by 98% sulphuric acid to give fuming sulphuric acid of oleum.

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7$$

Sulphuric acid of desired concentration can be prepared by diluting the oleum with water.

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

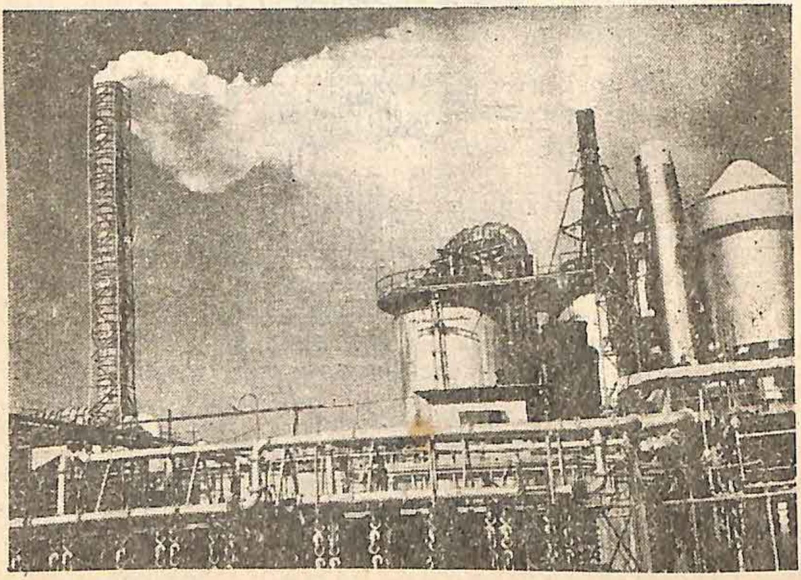
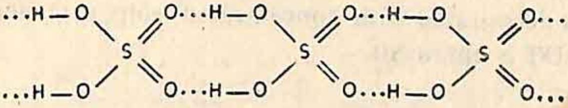


Fig. 9.13. A photograph showing sulphuric acid plant.

Properties

Pure sulphuric acid is a colourless, viscous liquid (density=1.84 g cm^{-3} at 288K) which boils at 513K.. Its high boiling point and viscosity are presumably because of hydrogen bonding:



The chemical properties of sulphuric acid may be studied under these heads:

(i) Acid properties (ii) Dehydrating properties
(iii) Oxidizing properties (iv) Miscellaneous reactions

ACID PROPERTIES

In aqueous solution, sulphuric acid behaves as a strong acid. Its ionization takes place in the following two steps:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$
$$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$$

It exhibits typical properties of an acid, SO_4^{2-} ions and HSO_4^- ions.

It neutralizes alkalies and reacts with metals to form salts:

$$NaOH + H_2SO_4 \longrightarrow NaHSO_4 + H_2O$$
$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Its sulphate ions react with barium ions and lead ions to form white precipitate of barium sulphate and lead sulphate, respectively.

DEHYDRATING PROPERTIES

It has a strong affinity for water and is thus used as a dehydrating agent. It removes water from many organic compounds like formic acid, oxalic acid, glucose, etc.

$$HCOOH \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CO$$

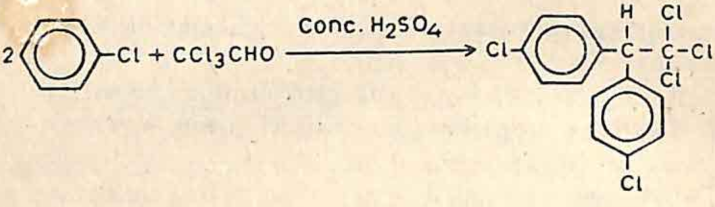
$$\underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\ |\\ COOH\end{array}} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CO + CO_2$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[-6H_2O]{\text{Conc. } H_2SO_4} 6C$$

This property of the acid is used in the manufacture of many important compounds. For example, ether is manufactured by the dehydration of alcohol.

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5}$$

When a mixture of chlorobenzene and trichloroacetaldehyde (chloral) is dehydrated with concentrated sulphuric acid, the insecticide DDT is obtained:



DDT

The dehydrating action of sulphuric acid is used in drying the gases which do not react with the acid like chlorine, sulphur dioxide, hydrogen chloride, etc.

OXIDIZING PROPERTIES

Hot concentrated sulphuric acid acts as a powerful oxidizing agent. It oxidizes non-metals like carbon, phosphorus, sulphur, etc.

$$C+2H_2SO_4 \longrightarrow CO_2+2SO_2+2H_2O$$
$$2P+3H_2SO_4 \longrightarrow 2H_3PO_4+3SO_2$$
$$S+2H_2SO_4 \longrightarrow 3SO_2+2H_2O$$

HBr, HI and H_2S are oxidized to bromine, iodine and sulphur, respectively.

$$2HX+H_2SO_4 \longrightarrow X_2+SO_2+2H_2O$$
$$(\text{where } X = \text{Br or I})$$

$$3H_2S+H_2SO_4 \longrightarrow 4H_2O+4S$$

MISCELLENEOUS REACTIONS

Sulphuric acid reacts with nitrates and chlorides to form nitric acid and hydrochloric acid which are more volatile than itself.

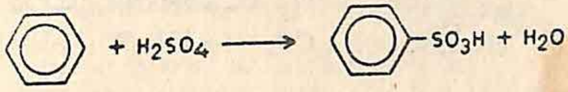
$$NO_3^-+H_2SO_4 \longrightarrow HSO_4^-+HNO_3$$
$$Cl^-+H_2SO_4 \longrightarrow HSO_4^-+HCl$$

Sulphuric acid reacts with phosphorus pentachloride when one or both of its hydroxyl groups are replaced by chlorine atoms.

$$\mathrm{HO{-}SO_2{-}OH + PCl_5 \longrightarrow \underset{\text{Chlorosulphonic acid}}{HO{-}SO_2{-}Cl} + POCl_3 + HCl}$$

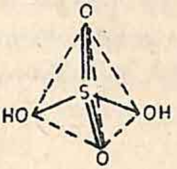
$$\mathrm{HO{-}SO_2{-}Cl + PCl_5 \longrightarrow \underset{\text{Sulphuryl chloride}}{Cl{-}SO_2{-}Cl} + POCl_3 + HCl}$$

Many organic compounds are sulphonated when treated with concentrated sulphuric acid. For example:



Structure

The molecule of sulphuric acid has a tetrahedral structure with a 6-valent sulphur.



Uses

It is one of the most important chemicals which is used in a large number of industries. Some of its uses are:

(i) In fertilizer industry for the manufacture of ammonium sulphate and superphosphate of lime.
(ii) In the manufacture of dyes, drugs and disinfectants.
(iii) In refining petroleum and in coal tar industry.
(iv) In paper, textile, leather and rubber industries.
(v) In the manufacture of important chemicals like hydrochloric acid, nitric acid, phosphoric acid, alums, sulphates, ether, etc.
(vi) In storage batteries.
(vii) In the manufacture of explosives like T.N.T., dynamite, nitroglycerine, etc.
(viii) In the manufacture of paints and pigments.
(ix) In metallurgical operations.
(x) For *pickling* (removing the basic oxide layer) of metal surfaces before treatment.
(xi) As a dehydrating and drying agent.
(xii) As an important reagent in the laboratory.

(xiii) In the manufacture of synthetic fibres like rayon and in plastic industry.
(xiv) In the manufacture of detergents.

9.6. SODIUM SULPHITE

The compound sodium sulphite, $Na_2SO_3.7H_2O$, is prepared by treating sodium carbonate solution with sulphur dioxide gas.

$$Na_2CO_3+H_2O+2SO_2 \longrightarrow 2NaHSO_3+CO_2$$
$$2NaHSO_3+Na_2CO_3 \longrightarrow 2Na_2SO_3+H_2O+CO_2$$

Properties

It forms colourless, monoclinic crystals soluble in water.

With acids, it decomposes to give sulphur dioxide.

$$SO_3^{2-}+2H^+ \longrightarrow SO_2+H_2O$$

With bromine water, it is oxidized to sulphate.

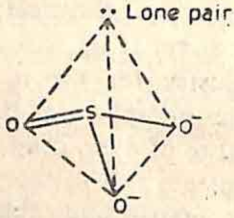
$$SO_3^{2-}+H_2O+Br_2 \longrightarrow SO_4^{2-}+2HBr$$

Its aqueous solution is a good reducing agent.

$$SO_3^{2-}+H_2O \longrightarrow SO_4^{2-}+2H^++2e^-$$

Structure

The X-ray analysis of sodium sulphite crystal reveals that sulphite ion has a pyramidal structure.



Uses

The important uses of sodium sulphite are:

(i) As a source of sulphur dioxide which is a strong disinfectant (for air) and mild bleaching agent (for silk, wool and sugar).
(ii) In the preparation of photographic developers.
(iii) As an antiseptic.
(iv) As an antichlor.
(v) As a preservative for food-stuffs.

(vi) As an addition compound to boiler-feed water for checking the scale formation and corrosion.

9.7. SODIUM BISULPHITE

It is prepared by passing sulphur dioxide through a saturated solution of sodium sulphite.

$$Na_2SO_3+SO_2+H_2O \longrightarrow \underset{\text{Sodium bisulphite}}{2NaHSO_3}$$

Sodium bisulphite is used as an antichlor and as a reducing agent. It is also used in the manufacture of dyes and of iodine.

9.8. SODIUM METABISULPHITE

This compound ($Na_2S_2O_5$) is obtained when sodium bisulphite is dehydrated by careful heating at a controlled temperature.

$$2NaHSO_3 \longrightarrow Na_2S_2O_5+H_2O$$

The important uses of sodium metabisulphite are:

(i) In textile industry as a bleaching agent and as an antichlor.
(ii) In tanning industry as a reducing agent.
(iii) In photography.
(iv) As a preservative for fruits.
(v) In the manufacture of hydrosulphite solutions.

EXERCISES

9.1 Name the elements of the oxygen family and give their electronic configurations.
9.2 Why are the elements of the oxygen family called chalcogens ? Discuss general trends in their physical properties.
9.3 Why does the tendency to show −2 oxidation state decrease as we move down the group VIA of the Periodic Table ?
9.4 Explain the formation of hexavalent sulphur compounds.
9.5 Why does oygen exhibit anomalous behaviour ?
9.6 Why are the melting and boiling points of water exceptionally higher compared to those of the hydrides of sulphur, selenium and tellurium ?
9.7 How is ozone prepared ? Draw its structure and explain.
9.8 How is ozonolysis used to locate the position of carbon-carbon double bond in unsaturated organic compounds ?
9.9 Discuss important properties and uses of ozone.
9.10 Describe contact process for the manufacture of sulphuric acid.

9.11 How are the dehydrating properties of sulphuric acid made use in the industry ? Give appropriate examples.

9.12 Give the structure of sulphuric acid. How will you show that it contains two hydroxyl groups ?

9.13 What are the important uses of sulphuric acid ?

9.14 How is sodium sulphate prepared ? Give its properties and uses,

9.15 How will you obtain sodium metabisulphite from sodium bisulphite ? Give the uses of sodium metabisulphite.

Unit 10

The Halogen Family

Electronic structure and trends in properties. Positive oxidation states of halogens. Preparation, properties and uses of fluorine and hydrogen fluoride. Fluorocarbons. Preparation and uses of bleaching powder and sodium hypochlorite.

The halogen family (Group VIIA) comprises highly reactive elements—fluorine, chlorine, bromine, iodine and the short-lived radioactive astatine. The name *halogen* is derived from Greek which means sea salts producer (*halos*=sea salts, *genes*=born). These elements, with the exception of astatine, occur extensively in the form of salts in sea water and other places.

10.1. GENERAL TRENDS

The halogens are characterized with the electronic configuration of ns^2np^5 (Table 10.1). They have only one electron less than the number present in the adjacent noble gas. Thus they show a strong tendency to complete the octet and acquire the stable noble gas configuration. This is achieved either by taking up an electron from metals to form ionic compounds or by sharing an electron with electron with non metals to form covalent compounds.

All the halogens form diatomic molecules. They are coloured because they absorb light in the visible region resulting in the excitation of outer electrons to higher energy levels. The smaller the atom, more will be the energy needed for excitation. Gaseous F_2 molecules absorb *high energy* violet light and appear yellow while gaseous I_2 molecules absorb *low energy* yellow light and appear violet. Similarly, chlorine molecules appear yellowish-green and bromine molecules reddish-brown.

TABLE 10.1: Some Properties of the Halogens

Element	*Atomic number*	*Electronic configuration*	*Electron affinity, kJ/mol*	*Abundance in earth's crust, ppm*
F	9	[He] $2s^22p^5$	333	900
Cl	17	[Ne] $3s^23p^5$	348	314*
Br	35	[Ar] $3d^{10}4s^24p^5$	340	1.6
I	53	[Kr] $4d^{10}5s^25p^5$	297	0 3

*15 000 ppm in sea water.

The halogens show a general gradation in their properties. Their typical non-metallic character gradually decreases down the group and iodine shows some metallic character. It has a metallic lustre and can exist as positive ion in ICl or ICN.

$$ICl \rightleftharpoons I^+ + Cl^-$$

$$ICN \rightleftharpoons I^+ + CN^-$$

As expected, atomic and ionic radii (Fig. 10.1) densities (Fig. 10.2) and melting and boiling points (Fig. 10.3) increase steadily from fluorine to iodine. The ionization energies (Fig. 10.4) and electronegativities (Fig. 10.5) are very high and decrease gradually from fluorine to iodine. The electron affinities of the elements are very high (Table 10.1).

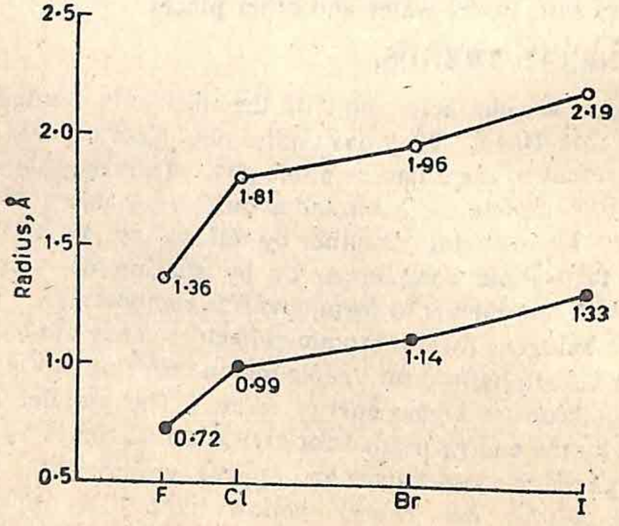


Fig. 10.1. Atomic (●) and ionic(O) radii of halogens.

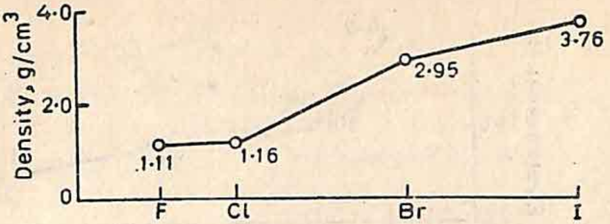


Fig. 10.2. Densities of halagens.

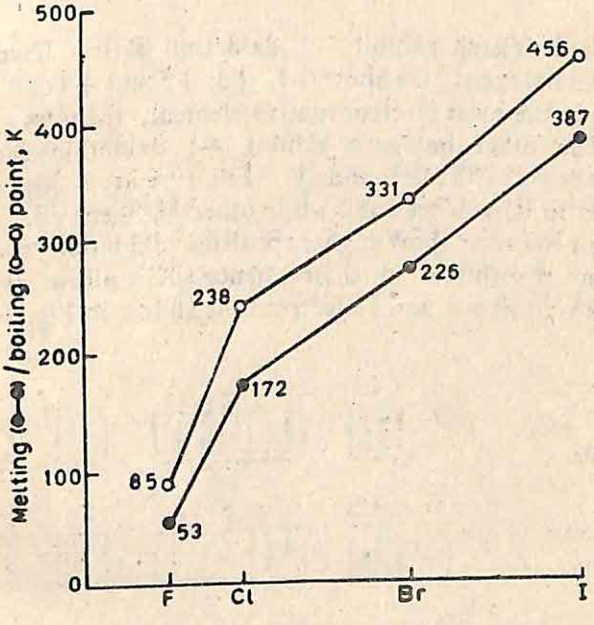


Fig. 10.3. Melting and boiling points of halogens.

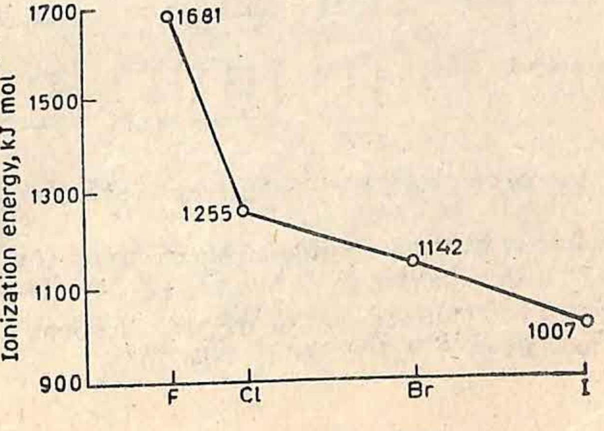


Fig. 10.4. Ionization energies of halogens.

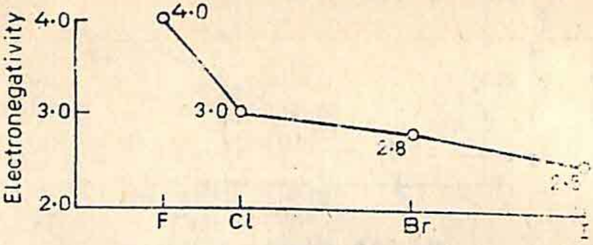


Fig. 10.5. Electronegativities of halogens.

All the halogens exhibit −1 oxidation state. Except fluorine, rest of the halogens also show +1, +3, +5 and +7 oxidation states. Fluorine is the most electronegative element, it shows −1 oxidation state. The other halogens exhibit +1 oxidation state in fluoro compounds like ClF, BrF and IF. Fluorine atom does not possess *d* orbitals in its valence shell while other halogens do. This is why all, except fluorine, show higher positive oxidation states because the vacant *d* orbitals in their valence shells allow easy excitation of *p*− as well as *p*− and *s*-electrons, as shown in Fig. 10.6.

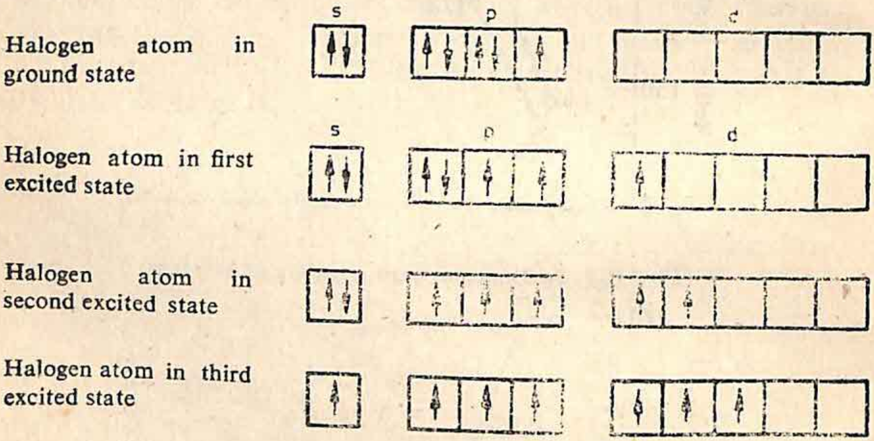
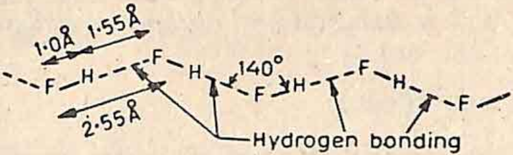

s
p
d
Halogen atom in ground state
Halogen atom in first excited state
Halogen atom in second excited state
Halogen atom in third excited state

Fig. 10.6. Variable oxidation states shown by the halogens.

Because of its small size and highly electronegative nature, fluorine is hydrogen bonded in its hydride, i.e., HF. This explains why the melting and boiling points of HF are exceptionally higher compared to those of HCl, HBr and HI (Fig. 10.7).



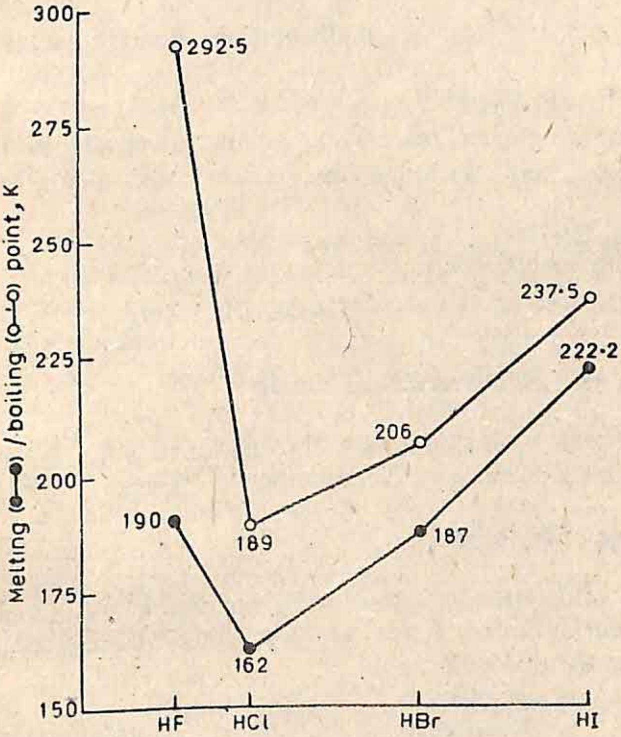


Fig. 10.7. Comparison of boiling points and melting points of hydrogen halides

Oxidizing Action

Halogens show a great tendency to pick up electrons because of their high electron affinities. Thus they act as strong oxidizing agents. However, the oxidizing power decreases on descending the group. Fluorine is highly oxidizing and oxidizes water to oxygen and ozone.

$$2F_2+2H_2O \longrightarrow 4HF+O_2$$
$$3F_2+3H_2O \longrightarrow 6HF+O_3$$

The reactions with chlorine and bromine are less vigorous.

$$X_2+H_2O \longrightarrow HX+HOX$$
(where X=Cl or Br)

Iodine is an even weaker oxidizing agent and scarcely reacts with water. At low temperatures, the crystals of halogen hydrates, $X_2 . nH_2O$, are obtained.

Reaction with Alkalies

Fluorine reacts with a 2% alkali solution to form oxygen difluoride OF_2.

$$2F_2+2OH^- \longrightarrow 2F^-+H_2O+OF_2$$

With hot and concentrated alkali solution, fluorine yields fluoride and oxygen.

$$2F_2+4OH^- \longrightarrow 4F^-+2H_2O+O_2$$

The other halogens react with cold and dilute alkali solution to give hypohalites. With hot and concentrated alkali, halates are obtained.

$$\underset{\text{(Cold and dil. alkali)}}{X_2+2OH^-} \longrightarrow H_2O+X^-+\underset{\text{Hypohalite ion}}{XO^-}$$

$$\underset{\text{(Hot and conc. alkali)}}{3X_2+6OH^-} \longrightarrow 3H_2O+5X^-+\underset{\text{Halate ion}}{XO_3^-}$$

Reaction with Metals and Non-Metals

Halogens react with metals as well as non-metals to form halides. The reactivity decreases as we descend the group.

Estimation of Halogens

Iodine is volumetrically estimated by titration with sodium thiosulphate solution using starch as indicator. A deep blue colour appears at the end point.

$$I_2+\underset{\text{Thiosulphate}}{2S_2O_3^{2-}} — 2I^-+\underset{\text{Tetrathionate}}{S_4O_6^{2-}}$$

Small amounts of chlorine and bromine present in a solution can also be estimated by reacting them with potassium iodide. The liberated iodine is then titrated with thiosulphate solution.

$$X_2+2KI — 2KX+I_2 \text{ (where } X=Cl \text{ or } Br)$$

10.2. OCCURRENCE OF HALOGENS

The halogens are very reactive and hence they do not occur free in nature. In combined form fluorine occurs as insoluble CaF_2 (fluorspar), Na_3AlF_6 (cryolite) and $3Ca_3(PO_4)_2.CaF_2$ (fluorapatite). Chlorine and bromine occur as chlorides and bromides in sea water and underground brines. Sodium chloride also occurs as rock salt. Some sea weeds and sponges contain iodine as iodides. Chile saltpeter ($NaNO_3$) contains about 0.2% iodine in the form of sodium iodate, $NaIO_3$.

10.3. USES OF HALOGENS

Fluorine is a very strong oxidizing agent and is used as a rocket fuel. Fluorocarbons are extremely inert and stable and find use as refrigerant gases (like *Freon-12* CF_2Cl_2) and in manufacturing heat-resistant plastics (like *Teflon*, polymerized C_2F_4). The isotopes of uranium can be separated by gaseous diffusion of UF_6.

Chlorine is the most useful among halogens. It is extensively used for the manufacture of a very large variety of organic chemicals which include solvents like chloroform and carbon tetrachloride, plastics like PVC, insecticides like DDT, germicides, drugs, dyes, refrigerants, etc. Chlorine is used for sterilizing water and as a bleaching agent for wood pulp, cotton and rayon.

Bromine is used in the manufacture of silver bromide which forms the basis of photographic films. The bromine compound 1,2-dibromoethane is added to petrol to remove lead as volatile lead bromide. Some bromine preparations are used as drugs.

A familiar use of iodine is in the form of its alcoholic solution, tincture iodine (antiseptic). Iodine is used in the manufacture of silver iodide (used in photographic films), dyes (used in colour photography) and some preparations like iodized salt.

10.4. HYDROGEN HALIDES

All the halogens react with hydrogen to form hydrogen halides, HX. The reaction between fluorine and hydrogen is violent while that between iodine and hydrogen is very slow at room temperature. This illustrates the decreasing reactivity of halogens on descending the group.

HF and HCl can be prepared by treating fluorides and chlorides with concentrated sulphuric acid.

$$CaF_2+H_2SO_4 \longrightarrow CaSO_4+2HF$$

$$NH_4Cl+H_2SO_4 \longrightarrow NH_4HSO_4+HCl$$

$$NaCl+H_2SO_4 \longrightarrow NaHSO_4+HCl$$

HBr and HI cannot be prepared by similar treatment of bromides or iodides with sulphuric acid. This is because H_2SO_4 oxidizes HBr and HI to bromine and iodine, respectively. These halides are prepared by hydrolysis of phosphorus trihalides with cold water (Fig. 10.8).

$$2P + 3X_2 \longrightarrow 2PX_3$$

$$PX_3 + 3H_2O \longrightarrow H_3PO_3 + 3HX$$

(where X=Br or I)

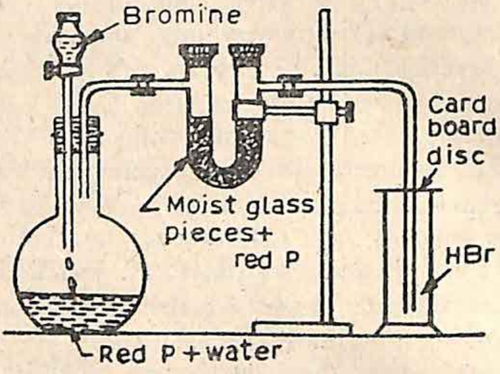


Fig. 10.8. Preparation of HBr.

HF is a liquid while HCl, HBr and HI are gases. This **anomalous** behaviour of HF is due to hydrogen bonding and also explains its exceptionally high melting and boiling points (Fig. 10.7). In the gaseous state, the hydrogen halides are covalent. In aqueous solutions, they ionize and function as strong acids.

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

10.5. OXIDES AND OXYACIDS OF HALOGENS

Most of the halogen oxides are unstable and explosive. The iodine oxides are the most stable. In general, the halogen oxide in which halogen is in higher oxidation state is more stable. Because of the small difference in electronegativities of halogen and oxygen, the compounds are usually covalent; I_2O_4 and I_4O_9 are ionic and can be represented as $IO^+ . IO_3^-$ and $I^{3+} . (IO_3^-)_3$, respectively. Since fluorine is more electronegative than oxygen, their binary compounds should better be called as oxygen fluorides rather than fluorine oxides. The halogen oxides (and oxygen fluorides) are listed in Table 10.2.

TABLE 10.2: Halogen Oxides

Oxygen fluorides	*Chlorine oxides*	*Bromine oxides*	*Iodine oxides*
$OF_2(g)$	Cl_2O (g)	Br_2O (g)	I_2O_4 or $IO^+.IO_3^-$ (s)
O_2F_2 (s), stable below 178K	ClO_2 (g)	BrO_2 (s), stabe blow 233K	I_2O_5, most stable oxide, white solid
	Cl_2O_6, red liquid	BrO_3 (s), stable below 203K	I_4O_9 or $I^{3+}.(IO_3^-)_3$, yellow solid
	Cl_2O_7 (l)		

Chlorine, bromine and iodine form four series of oxyacids—HOX (hypohalous acid), HXO_2 (halous acid), HXO_3 (halic acid) and HXO_4 (perhalic acid)—in which the oxidation states of halogens are $+1$, $+3$, $+5$ and $+7$, respectively. The names of oxyacids of chlorine and their corresponding sodium salts are given below:

Chlorine oxyacid	*Sodium salt*
HOCl Hypochlorous acid	NaOCl Sodium hypochlorite
$HClO_2$ Chlorous acid	$NaClO_2$ Sodium chlorite
$HClO_3$ Chloric acid	$NaClO_3$ Sodium chlorate
$HClO_4$ Perchloric acid	$NaClO_4$ Sodium perchlorate

Oxyacids and their salts are used as oxidizing agents and as laboratory reagents. Sodium chlorate is used in fireworks and in matches (as oxidizing agent). Potassium iodate, KIO_3, is used as primary standard in iodometric titrations. In acid solution, it reacts with potassium iodide and liberates iodine quantitatively:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

10.6. POSITIVE OXIDATION STATE OF HALOGENS

The metallic character always increases as we descend a group. Fluorine is the most electronegative element, always shows -1 oxidation state and has no tendency to form positive ions. If the interhalogen compound, ClF, tends to ionize, it will form Cl^+ and F^- because of higher electronegativity of fluorine. In bromine compounds, BrF_3 and Br (pyridine) NO_3, bromine exists as positive bromine. The compounds having I^+ and I^{3+} are still better established. Molten ICl, molten ICN (in pyridine) and $I(CH_3COO)_3$ ionize as shown below:

$$2ICl \rightleftharpoons ICl_2^- + I^+ \text{ (At cathode)}$$
$$ICN \rightleftharpoons CN^- + I^+ \text{ (At cathode)}$$
$$I(CH_3COO)_3 \rightleftharpoons 3CH_3COO^- + I^{3+} \text{ (At cathode)}$$

10.7. FLUORINE

Fluorine is prepared by electrolysis of a fused solution of KHF_2 in a V-shaped vessel of copper, nickel or steel using a graphite anode and a steel cathode (Fig. 10.9). The electrolysis is carried out at about 370K at which a mixture of KF in HF (ratio 1:2-3) melts.

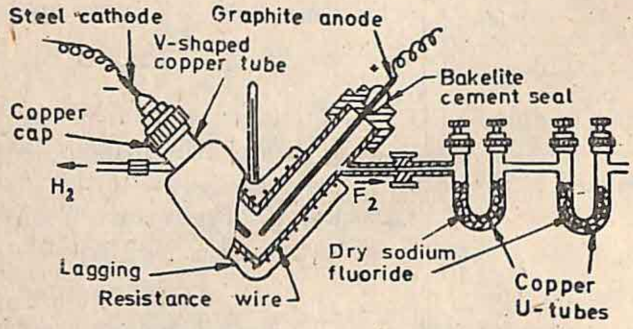


Fig. 10.9. Preparation of fluorine.

The potential required for the discharge of F ions is the highest, other anions if present, will be discharged in preference to F ions. Even the traces of water, if present, can react with fluorine to give oxygen. Thus, the electrolyte must be free from any other anions or moisture.

In another cell, used for commercial production of fluorine (Fig. 10.10), a 90% solution of KHF_2 in anhydrous HF is used as

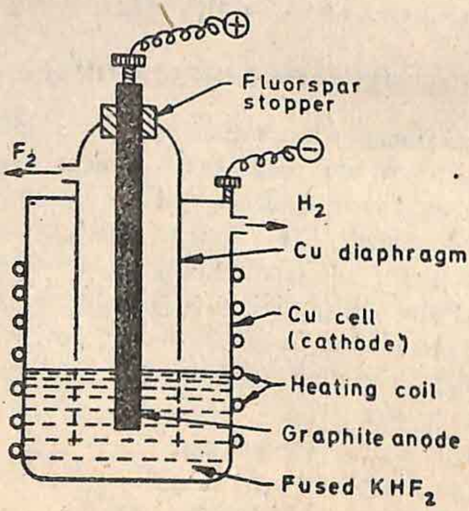


Fig. 10.10. Commercial production of fluorine

trolyte. The cell is electrically heated and is made of copper or steel which also serves as cathode while anode is made of copper mixed graphite. A copper diaphragm is used to separate the electrodes.

The fluorine obtained is quite pure and is compressed in steel cylinders.

Properties

Fluorine is highly reactive element owing to its highest electronegativity (Fig. 10.5), smallest size (Fig. 10.1) and very low bond dissociation energy (Fig. 10.11). It directly reacts with practically all elements except nitrogen and oxygen.

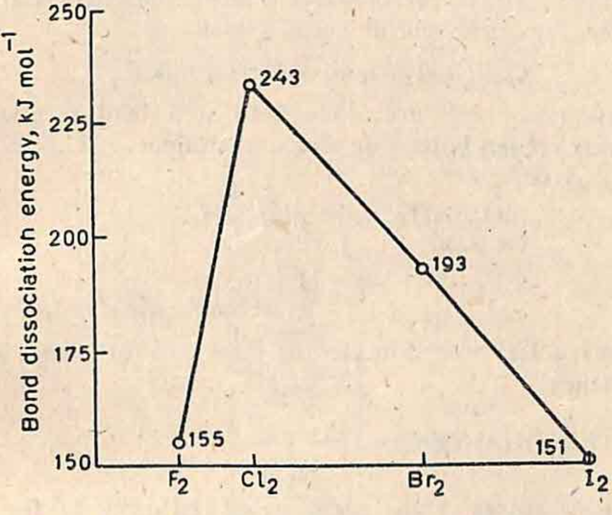


Fig. 10.11. Bond dissociation energies of halogens.

Fluorine reacts with hydrogen violently, even in darkness and at low temperature.

$$F_2+H_2 \longrightarrow 2HF$$

It reacts with all metals forming fluorides. For example:

$$2Na+F_2 \longrightarrow 2NaF$$

$$Ca+F_2 \longrightarrow CaF_2$$

Non-metals like carbon, silicon, phosphorus, sulphur, etc., react with fluorine and form the highest fluorides.

$$Si+2F_2 \longrightarrow SiF_4$$

$$S+3F_2 \longrightarrow SF_6$$

Hydrocarbons react vigorously with fluorine. However, the reaction can be controlled by dilution of fluorine with nitrogen.

Under such conditions and in presence of copper fluoride catalyst at 430-625K, *fluorocarbons* (i.e., fluorinated hydrocarbons) like CHF_3, CH_2F_2, CH_3F, CF_4, C_2F_8 and C_3F_3 are obtained. These compounds are extremely inert and find applications as refrigerants, solvents, lubricants, plastics, etc.

10.8. HYDROGEN FLUORIDE

Anhydrous hydrogen fluoride can be prepared in the laboratory by heating dry potassium fluoride in a copper retort connected with a copper condenser.

$$KHF_2 \longrightarrow KF+HF$$

Industrially, HF is obtained by heating fluorspar (CaF_2) with concentrated sulphuric acid in a lead vessel.

$$CaF_2+H_2SO_4 \longrightarrow CaSO_4+2HF$$

The vapours of HF are condensed in a lead receiver. It is stored in wax coated bottles or plastic containers. This is because HF attacks glass.

$$\underset{\text{(In glass)}}{SiO_2}+4HF \longrightarrow SiF_4+2H_2O$$

$$SiF_4+2HF \longrightarrow \underset{\text{Hydrofluosilicic acid (soluble)}}{H_2SiF_6}$$

This action of HF is used in etching glass and for removing silica from substances.

10.9. INTERHALOGENS

Each halogen reacts with every other halogen to form compounds known as *interhalogens* or *interhalogen compounds*. They are of four types AX, AX_3, AX_5 and AX_7 (where A and X are different halogen atoms). These can be prepared by direct combination of the halogens. For example:

$$\underset{\text{(Equal volumes)}}{Cl_2 + F_2} \longrightarrow 2ClF$$

$$Cl_2 + \underset{\text{(In excess)}}{3F_2} \longrightarrow 2ClF_3$$

$$Br_2 + \underset{\text{(In excess)}}{5F_2} \longrightarrow 2BrF_5$$

Interhalogens are more reactive than elemental halogess except fluorine. This is because A-X bond energy is less than the A-A or X-X bond energy.

10.10. POLYHALIDES

Polyhalide ions are formed when halide ions associate with halogens or interhalogens. For example, elemental iodine reacts with iodide ions to form soluble polyhalide triodide ions. This explains the solubility of iodine in potassium iodide.

$$I_2 + I^- \longrightarrow I_3^-$$

Fluorine does not form polyhalide ions because it has no available *d* orbitals and cannot expand its octet.

10.11. BLEACHING POWDER

Bleaching powder, $CaOCl_2$, is prepared by passing dry chlorine over dry slaked lime, $Ca(OH)_2$, at 303-311K (Fig. 10.12).

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{CaOCl_2 + H_2O}$$

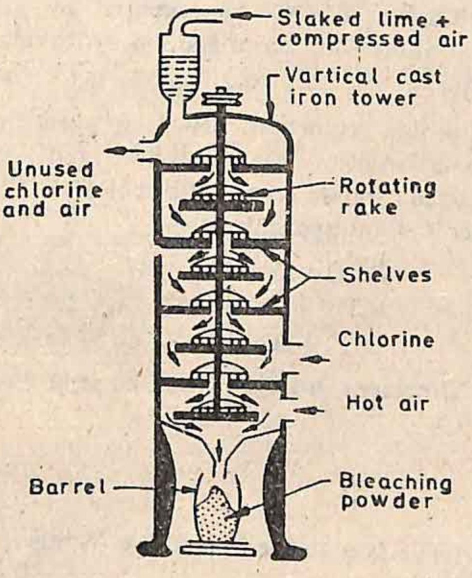


Fig. 10.12. Manufacture of bleaching powder.

Properties

It is a yellowish white powder and gives a strong smell of chlorine. In presence of small amount of dilute acid, it can act as an oxidizing and bleaching agent.

$$2CaOCl_2 + 2H^+ \longrightarrow CaCl_2 + 2HCl + 2(O)$$

Under such conditions and in presence of copper fluoride catalyst at 430-625K, *fluorocarbons* (i.e., fluorinated hydrocarbons) like CHF_3, CH_2F_2, CH_3F, CF_4, C_2F_8 and C_3F_3 are obtained. These compounds are extremely inert and find applications as refrigerants, solvents, lubricants, plastics, etc.

10.8. HYDROGEN FLUORIDE

Anhydrous hydrogen fluoride can be prepared in the laboratory by heating dry potassium fluoride in a copper retort connected with a copper condenser.

$$KHF_2 \longrightarrow KF + HF$$

Industrially, HF is obtained by heating fluorspar (CaF_2) with concentrated sulphuric acid in a lead vessel.

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

The vapours of HF are condensed in a lead receiver. It is stored in wax coated bottles or plastic containers. This is because HF attacks glass.

$$\underset{\text{(In glass)}}{SiO_2} + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2HF \longrightarrow \underset{\text{Hydrofluosilicic acid (soluble)}}{H_2SiF_6}$$

This action of HF is used in etching glass and for removing silica from substances.

10.9. INTERHALOGENS

Each halogen reacts with every other halogen to form compounds known as *interhalogens* or *interhalogen compounds*. They are of four types AX, AX_3, AX_5 and AX_7 (where A and X are different halogen atoms). These can be prepared by direct combination of the halogens. For example:

$$\underset{\text{(Equal volumes)}}{Cl_2 + F_2} \longrightarrow 2ClF$$

$$Cl_2 + \underset{\text{(In excess)}}{3F_2} \longrightarrow 2ClF_3$$

$$Br_2 + \underset{\text{(In excess)}}{5F_2} \longrightarrow 2BrF_5$$

Interhalogens are more reactive than elemental halogess except fluorine. This is because A-X bond energy is less than the A-A or X-X bond energy.

10.10. POLYHALIDES

Polyhalide ions are formed when halide ions associate with halogens or interhalogens. For example, elemental iodine reacts with iodide ions to form soluble polyhalide triodide ions. This explains the solubility of iodine in potassium iodide.

$$I_2+I^- \longrightarrow I_3^-$$

Fluorine does not form polyhalide ions because it has no available *d* orbitals and cannot expand its octet.

10.11. BLEACHING POWDER

Bleaching powder, $CaOCl_2$, is prepared by passing dry chlorine over dry slaked lime, $Ca(OH)_2$, at 303-311K (Fig. 10.12).

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$$

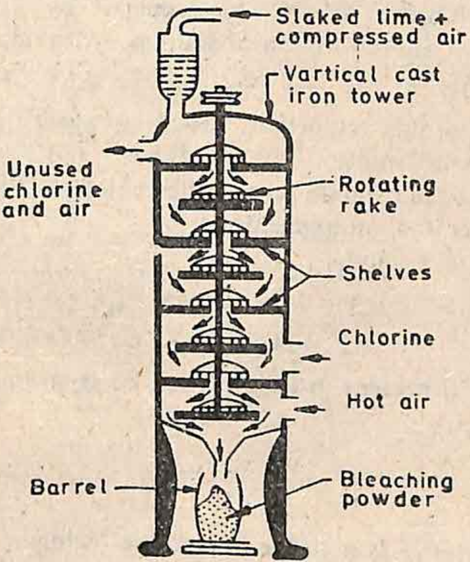


Fig. 10.12. Manufacture of bleaching powder.

Properties

It is a yellowish white powder and gives a strong smell of chlorine. In presence of small amount of dilute acid, it can act as an oxidizing and bleaching agent.

$$2CaOCl_2+2H^+ \longrightarrow CaCl_2+ 2HCl+2(O)$$

On treatment with an excess of a dilute acid or even carbon dioxide, bleaching powder liberates whole of its chlorine.

$$CaOCl_2 + 2H^+ \longrightarrow Ca^{2+} + H_2O + Cl_2$$
$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

The chlorine liberated on treatment of bleaching powder with acid is called *available chlorine.* A good sample of bleaching powder contains 35-38% of available chlorine.

Uses

Bleaching powder is mainly used for bleaching cotton, linen, jute and wood pulp. It is also used as a disinfectant and germicide for sterilizing water.

10.12. SODIUM HYPOCHLORITE

Sodium hypochlorite, NaOCl, is prepared by passing chlorine through cold and dilute solution of sodium hydroxide.

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

Commercially, this important bleaching agent is prepared by electrolysis of brine solution in an undivided cell. Sodium hydroxide liberated at the cathode reacts with chlorine liberated at the anode to produce sodium hypochlorite.

At cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$
At anode: $2Cl \longrightarrow Cl_2 + 2e^-$
$Cl_2 + 2OH^- \longrightarrow Cl^- + OCl^- + H_2O$

NaCl and NaOCl present in solution can be separated by fractional crystallization.

Properties

Sodium hypochlorite is alkaline in solution owing to the following reaction:

$$NaOCl + H_2O \longrightarrow HOCl + NaOH$$

As it can give out oxygen readily, sodium hypochlorite acts as a powerful oxidizing and bleaching agent. In acid solution it oxidizes iodide to iodine, Fe^{2+} to Fe^{3+}, etc.

$$2I^- + H^+ + NaOCl \longrightarrow I_2 + NaOH + Cl^-$$
$$2Fe^{2+} + H^+ + NaOCl \longrightarrow 2Fe^{3+} + Cl^- + NaOH^-$$

EXERCISES

10.1 Name the members of the halogen family and write their electronic configurations. Why are they called *halogens?*

10.2 Discuss the general features of the elements of group VIIA with special reference to anomalous behaviour of fluorine.

10.3 How do you explain the higher oxidation states shown by all halogens except fluorine?

10.4 Why does HF show exceptionally higher melting and boiling points compared to those of other hydrogen halides?

10.5 Explain why:
  (i) Fluorine is yellow and iodine is voilet.
  (ii) The halogens are strong oxidants.
  (iii) HF is hydrogen bonded.

10.6 Write the formulae of halogen oxides. Which one is the most stable among them?

10.7 Name the oxyacids of chlorine and their corresponding sodium salts.

10.8 How will you prove the existence of positive oxidation state of iodine?

10.9 How are fluorocarbons prepared? What are their uses?

10.10 How is fluorine isolated? What precautions are necessary to obtain it in the pure form?

10.11 How is HF prepared? Why is it not stored in glass containers?

10.12 Write short notes on the following:
  (i) Interhalogens.
  (ii) Polyhalides.
  (iii) Bleaching powder.
  (iv) Sodium hypochlorite.

10.13 How do the halogens occur and what are their uses?

Unit 11

Nuclear Chemistry

Radioactivity. Type of Radiation. Group displacement law. Half life. Carbon dating.

Atom is composed of a nucleus surrounded by extranuclear electrons. The chemical behaviour of an element is governed by the electrons. The nucleus, except for its charge which influences the electrons, takes no part in the chemical activity. The change of nucleus to another nucleus means transformation of one substance into another (called *transmutation*). All nuclear changes are accompanied by emission of certain rays. This emission is called *radioactivity* and the substance emitting the rays is called *radioactive.* In *nuclear chemistry*, we deal with the nuclear changes with special emphasis on the chemical aspects. In this Unit, we shall deal with some aspects of this subject.

11.1. RADIOACTIVITY

Henry Becquerel, in 1896, observed that a uranium salt which was accidently left over a well wrapped photographic plate, had affected or fogged the plate. Dark shadow marks showing the outline of the pile of the salt appeared when the plate was developed. Further investigation showed that the element uranium present in the uranium salt was responsible for emitting rays which had affected the plate. The phenomenon was called *radioactivity* and the substance emitting the radiations was called *radioactive.* The radioactive emanation is completely unaffected by physical and chemical conditions. Marie Curie, in 1898, isolated the element radium from pitchblende mineral and this element was very highly radioactive compared to uranium. These naturally occurring radioactive ments can also induce radioactivity in other substances. The phenomenon is called *induced* or *artificial* radioactivity.

11.2. TYPES OF RADIATIONS

There are three principal types of rays associated with radioactive substances. They are:

(i) Alpha (α) rays,
(ii) Beta (β) rays and
(iii) Gamma (γ) rays.

Alpha Rays

In electric (Fig. 11.1) and magnetic (Fig. 11.2) fields, alpha rays bend only a little in one direction because of their heavy mass and large momentum. They consist of two protons and two neutrons, and are thus actually *helium nuclei* (helium atoms without their electrons). An α-ray (denoted by ${}^{4}_{2}\mathrm{He}$ or ${}^{4}_{2}\alpha$) moves with a velocity of 10 000-20000 miles per second. Inspite of the high velocity, they are not very penetrating because of their heavy mass. They can be stopped by an aluminium foil having thickness of less than 0.1 mm. On collision with gas molecules, α-particles knock out some electrons and produce ionized molecules.

Beta Rays

In electric and magnetic fields, β-rays bend heavily in opposite direction to that of α-rays (Figs. 11.1 and 11.2). This shows that they are negatively charged, possess negligible mass and smaller momentum. They are electrons (denoted by (${}^{0}_{-1}\mathrm{e}$ or ${}^{0}_{-1}\beta$) moving with velocity close to that of light and are about 100 times more penetrating than α-rays. Because of their small size, they ionize the gas to a small extent only.

Gamma Rays

They are electromagnetic radiations similar to radiowaves or light waves except that their wavelengths are extremely short of the order of 0.1 nm or 1 Å. They are extremely penetrating and can penetrate 100 cm thick aluminium sheet. Being chargeless, and massless γ-rays are not deflected in an electric or magnetic field (Figs. 11.1 and 11.2). They are weak ionizers of gases.

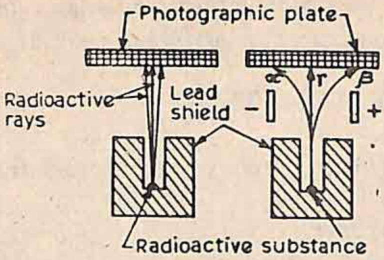


Fig. 11.1. Behaviour of α-, β- and γ-rays in electric field

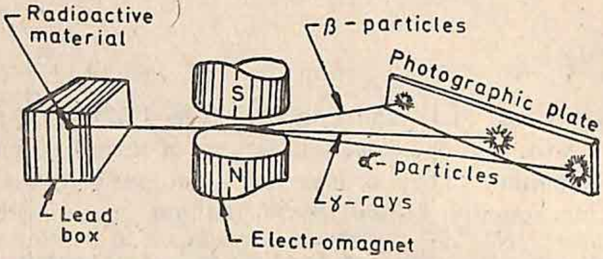


Fig. 11.2. Behaviour of α-, β and γ-rays in magnetic field.

Some less common forms of radioactive emissions include *neutrons*, *protons*, *positrons* (particles bearing a positive charge but having the same mass as an electron) and *deuterons* (particles containing a proton and a neutron).

11.3. GROUP DISPLACEMENT LAW

Radioactive emanation results into nuclear changes. It means transformation of one element into another and the process is called *transmutation*. When an alpha particle $\left({}^{4}_{2}\text{He} \right)$ is emitted, the new or *daughter* element has atomic number two units less than that of the original or parent element. The daughter element occupies a position two groups to the left of that of the parent element in the Periodic Table. When a beta particle (${}^{0}_{-1}\text{e}$) is emitted, the daughter element will have atomic number one unit more than that of the parent element. It will thus occupy a position one group to the right of that of the parent element in the Periodic Table. This is termed as the *group displacement law* and may be stated as: The emission of an alpha particle leads to the formation of an element which lies two positions to the left and the expulsion of a beta particle results in the formation of an element which lies one position to the right in the Periodic Table. The following examples serve as an illustration of the law.

Polonium ($^{215}_{84}Po$) belongs to group VIA of the Periodic Table. When it loses an alpha particle, it is transformed into radioactive lead ($^{211}_{82}Pb$), an element of group IVA. Thus, the daughter element occupies two places to the left of the parent element (Fig. 11.3).

$$^{215}_{84}Po \longrightarrow {}^{211}_{82}Pb + {}^{4}_{2}He$$

Radioactive lead ($^{211}_{84}Pb$), an element of group IVA, emits a beta particle and is transformed into radioactive bismuth ($^{211}_{83}Bi$) which belongs to group VA. It means that the daughter element has shifted one place to the right of the parent element (Fig. 11.3). Again, radioactive bismuth emits a beta particle and forms polonium ($^{211}_{84}Po$) which belongs to group VIA, *i.e.*, one position to the right of the parent element bismuth (Fig. 11.3).

$$^{211}_{82}Pb \longrightarrow {}^{211}_{83}Bi + {}^{0}_{-1}e$$

$$^{211}_{83}Bi \longrightarrow {}^{211}_{84}Po + {}^{0}_{-1}e$$

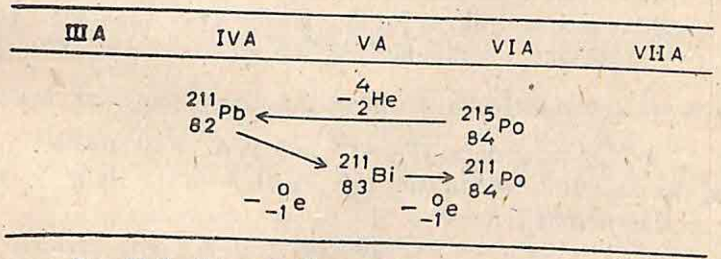


Fig. 11.3. Diagram illustrating group displacement law.

In the above examples, $^{215}_{84}Po$ and $^{211}_{84}Po$ are *isotopes* while $^{211}_{82}Pb$, $^{211}_{83}Bi$ and $^{211}_{84}Po$ are *isobars*. It may, therefore, be concluded that a beta particle emission results in the formation of an isobar while an isotope is produced as a result of the combined expulsion of one alpha particle and two beta particles.

The emission of γ-rays alone does not result in the formation of a new element. The mass number or the atomic number of the nucleus remains unchanged. In some nuclear reactions, the elements are produced in the excited states. These elements revert to the ground states by the emission of the excess energy in the form of γ-rays. Two examples of γ-emission are given below:

$$\underset{\text{(Excited state)}}{\left[{}^{125}_{52}\text{Te}\right]^*} \longrightarrow \underset{\text{(Ground state)}}{{}^{125}_{52}\text{Te}+\gamma}$$

$$\left[{}^{236}_{92}\text{U}\right]^* \longrightarrow {}^{236}_{92}\text{U}+\gamma$$

Example 11.1. From the following nuclear reactions, predict the positions of Po, Ta, Mg and C in the Periodic Table:

$$^{210}_{84}\text{Po} \longrightarrow {}^{206}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

$$^{186}_{73}\text{Ta} \longrightarrow {}^{186}_{74}\text{W} + {}^{0}_{-1}\text{e}$$

$$^{27}_{12}\text{Mg} \longrightarrow {}^{27}_{13}\text{Al} + {}^{0}_{-1}\text{e}$$

$$^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$

It is known that Pb, W, Al and N belong to groups IVA, VIA, IIIA and VA, respectively.

Solution. In the first reaction, $^{4}_{2}$He particle is emitted. It means that the parent element, Po, belongs to group VIA because the daughter element, Pb, is in the group IVA (daughter element lies two positions to the left of the parent element). In other reactions, $^{0}_{-1}$ e is emitted. It shows that the parent elements Ta, Mg and C belong to groups VA, IIA and IVA, respectively. In each case, the daughter element lies one position to the right of the corresponding parent element.

Example 11.2. Calculate the number of alpha and beta particles emitted when radioactive $^{232}_{90}$Th changes into $^{209}_{82}$Pb.

Solution. Change in mass number$=232-208=24$

Therefore, $^{4}_{2}$He particles emitted to account for this loss in mass number$=\frac{24}{4}=6$.

Expected decrease in atomic number due to emission of 6 α-particles$=6\times 2=12$

Expected atomic number of the daughter element$=90-12=78$.

Increase in atomic number required in order to achieve the actual atomic number of the daughter element$=82- -78=4$.

Therefore, number of $_{-1}^{0}e$ particles emitted to account for this increase=4

Hence, during the transformation of $^{232}_{92}$Th into $^{208}_{82}$Pb, the number of alpha and beta particles emitted are 6 and 4, respectively.

Example 11.3. $^{238}_{82}$U undergoes a series of changes emitting α- and β- particles and finally $^{206}_{82}$Pb is formed. Calculate the number of α- and β- particles which must have been ejected during the series.

Solution. Change in mass number=238—206=32

Therefore, $^{4}_{2}$He particles emitted$=\frac{32}{4}=8$.

Expected decrease in atomic number due to emission of 8 α-particles
=8×2=16

Expected atomic number of the final product=92—16=76

Increase in atomic number required to achieve the actual atomic number=82−76=6

Thus, number of $_{-1}^{0}e$ particles emitted to account for this increase=6

Hence, the number of α- and β-particles ejected during the series are 8 and 6, respettively.

11.4. CHEMICAL EQUATIONS FOR NUCLEAR CHANGES

In writing chemical equations for nuclear changes, we use a universally accepted system of notation. For an element E, its mass number (A) is written in the superscript while the atomic number (Z) is written in the subscript as $^{A}_{Z}E$. Some nuclear reactions are given below to explain the system of notation:

When nitrogen nuclei are bombarded with α-particles, we obtain oxygen and protons.

$$^{14}_{7}N + \ ^{4}_{2}He \longrightarrow \ ^{17}_{8}O + \ ^{1}_{1}H$$

Radioactive bromine is transformed to krypton emitting β-particles.

$$^{82}_{35}Br \longrightarrow \ ^{82}_{36}Kr + \ _{-1}^{0}e$$

Iron can capture an electron to give manganese.

$$_{-1}^{0}e + \ ^{55}_{26}Fe \longrightarrow \ ^{55}_{26}Mn$$

11.5. RADIOACTIVE DISINTEGRATION SERIES

In radioactive disintegration, a less stable nuclear species changes into a more stable one. The complete stability may be achieved by successive emission of α- and β-particles. Each Emission gives rise to a different element finally resulting into the most stable element which is no longer radioactive. Such a series involving transformations of parent radioactive element into the non-radioactive end and product is known as *radioactive disintegration series*. There are four such series and are called thorium (4n). neptunium (4n+1), uranium (4n+2) and actinium (4n+3) series. The neptunium or (4n+1) series is of man-made elements while others occur in nature. Mass numbers change only when α-particles ($^{4}_{2}He$) are emitted imparting a change of 4 units at each step·

In elements of 4n series, the mass numbers are divisible by 4. In (4n+1), (4n+2) and (4n+3) series, the mass numbers give remainders of 1, 2 and 3, respectively, when divided by 4. It is obvious that there can be only four disintegration series. Thorium (4n) series starts with $^{232}_{90}Th$ and ends with $^{208}_{82}Pb$, neptunium (4n+1) series starts with $^{241}_{94}Pu$ and ends with $^{209}_{83}Bi$, uranium (4n+2) series starts with $^{238}_{92}U$ and ends with $^{206}_{82}Pb$, and actinium (4n+3) series starts with $^{235}_{92}U$ and ends with $^{207}_{82}Pb$.

11.6. ARTIFICIAL TRANSMUTATIONS

It has been said earlier that the transmutation means the conversion of one element into another. In 1919, Rutherford reported the first artificial transmutation. He discovered that when α-particles (from $^{214}_{84}Po$) pass through nitrogen gas, very fast protons ($^{1}_{1}H$) originate and the product oxygen is formed. Thus:

$$^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$$

In the reaction, the *projectile* (α-particle, in this case) forms a compound nucleus with the *target* (nitrogen). The compound nucleus then rapidly ejects a *subsidiary* particle (proton) to form the *product* (oxygen).

In the following years, thousands of such transformations have been studied using different projectiles such as neutrons ($^{1}_{0}$n), deuterons ($^{2}_{1}$H), protons, etc., in addition to α-particles. Projectiles that bear a positive charge are repelled by targets. Various accelerators, such as *cyclotron* and *linear accelerator*, are used to impart sufficiently high kinetic energies to the positive projectiles to overcome the electrostatic repulsions of the targets.

The nuclear transformations are classified according to the nature of projectile and subsidiary particles. In Table 11.1, some transformations are listed.

TABLE 11.1. Some Nuclear Transformations

Type	*Nuclear transformation*
(α,n)	$^{75}_{33}As + ^{4}_{2}He \longrightarrow ^{78}_{35}Br + ^{1}_{0}n$
(p,n)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{7}_{4}Be + ^{1}_{0}n$
(n,p)	$^{45}_{21}Sc + ^{1}_{0}n \longrightarrow ^{45}_{20}Ca + ^{1}_{1}H$
(d,n)	$^{209}_{83}Bi + ^{2}_{1}H \longrightarrow ^{210}_{84}Po + ^{1}_{0}n$
(p,γ)	$^{14}_{7}N + ^{1}_{1}H \longrightarrow ^{15}_{8}O + \gamma$

d stands for deuteron.

11.7. DISINTEGRATION RATE AND DISINTEGRATION CONSTANT

A radioactive element is always disintegrating or decaying into fresh products. The rate of disintegration is not influenced by external factors such as temperature, pressure and chemical reactions. The number of atoms of a radioelement disintegrating in unit time, at any instance, is proportional to the number present. Thus:

$$-\frac{dN}{dt} \propto N$$

or

$$-\frac{dN}{dt} = \lambda N \tag{11.1}$$

where dN is the number of nuclei which decay during the time interval dt out of the N nuclei present at time t. λ is a proportionality constant and is called *disintegration* or *decay* constant. The negative sign indicates that N decreases with increase in t.

Equation (11.1) can be writen as :

$$\frac{dN}{dt} = -\lambda N$$

$$\text{or} \quad \frac{dN}{N} = -\lambda dt \tag{11.2}$$

On integration, we obtain :

$$\ln N = -\lambda t + C \tag{11.3}$$

where C is a constant of integration.

In the beginning at $t=0$, $N=N_0$. Substituting these values in the above equation, we get :

$$\ln N_0 = C \tag{11.4}$$

Combining equations (11.3) and (11.4), we obtain :

$$\ln N = -\lambda t + \ln N_0$$

$$\text{or} \quad \ln \frac{N}{N_0} = -\lambda t \tag{11.5}$$

$$\text{or} \quad \ln \frac{N_0}{N} = \lambda t$$

$$\text{or} \quad \lambda = \frac{1}{t} \ln \frac{N_0}{N}$$

Changing natural logarithms to common logarithms, we get :

$$\lambda = \frac{2.303}{t} \log \frac{N_0}{N} \tag{11.6}$$

Equation (11.5) can be written as :

$$\frac{N}{N_0} = e^{-t} \tag{11.7}$$

It follows from equation (11.7) that the number of radionuclei decreases exponentially with time.

11.8. HALF-LIFE PERIOD

It is the time required for a radioelement to decay to one-half its original value as is shown in Figs. 11.4 and 11.5. Half-life period is usually denoted by $t_{\frac{1}{2}}$. Each element has its characteristic $t_{\frac{1}{2}}$. For example, $t_{\frac{1}{2}}$ values of $^{238}_{92}\text{U}$, $^{230}_{90}\text{Th}$ and $^{226}_{88}\text{Ra}$ are 4.51×10^9 years, 8.0×10^4 years and 1.62×10^3 years, respectively. Fig. 11.6 shows the decay of 1 g sample of $^{128}_{53}\text{I}$ (half-life period=25 minutes) with time.

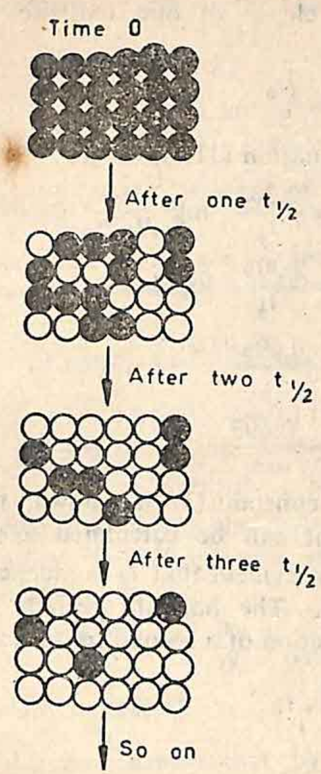


Fig. 11.4. A radioactive element decays to one-half its original value in one $t_{\frac{1}{2}}$.

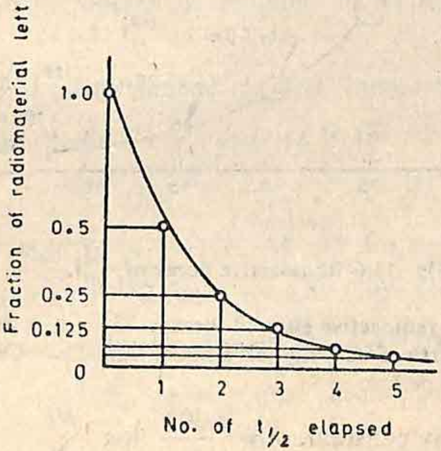


Fig. 11.5 Diagram showing exponential decay of a radioactive element.

It is evident that after the elapse of one half-life period, i.e., $t=t_{\frac{1}{2}}$, we obtain:

$$N=\frac{N_0}{2}$$

Substituting these values in equation (11.6), we get :

$$\lambda=\frac{2.303}{t_{\frac{1}{2}}}\ \log\frac{N_0}{N_0/2}$$

$$\lambda=\frac{2.303}{t_{\frac{1}{2}}}\ \log 2$$

$$\lambda=\frac{0.693}{t_{\frac{1}{2}}} \qquad (11.8)$$

Also, $$t_{\frac{1}{2}}=\frac{0.693}{\lambda} \qquad (11.9)$$

Thus, if the disintegration constant (λ) is known, the half-life period ($t_{\frac{1}{2}}$) of a radioelement can be calculated and *vice versa.* Since λ is a constant, it is evident that $t_{\frac{1}{2}}$ is independent of the amount of the radioelement. The half-life periods of different elements vary widely from fraction of a second to millions of years.

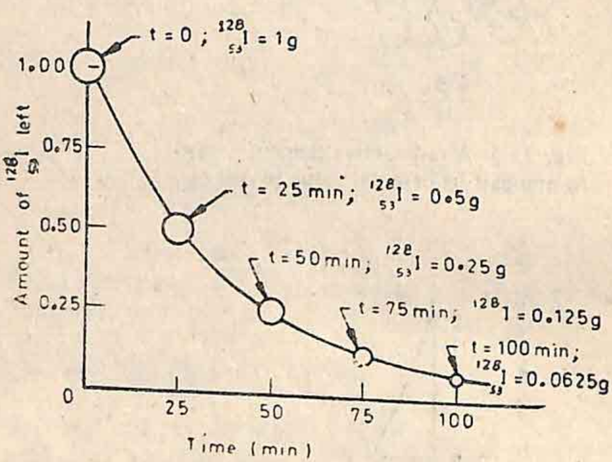


Fig. 11.6 Radioactive decay of $^{128}_{53}$I.

Example 11.4. A radioactive element decays at such a rate that after 68 minutes only one-fourth of its original amount remains. Calculate its decay constant and half-life period.

Solution. Decay constant, $\lambda=\frac{2.303}{t}\ \log\frac{N_0}{N}$

It is given that $t=68$ min; $N_0=1$; $N=\frac{1}{4}$

Substituting these values in the equation, we get:

$$\lambda = \frac{2.303}{68} \log \left(\frac{1}{1/4}\right)$$

$$\lambda = \frac{2.303 \times 0.6021}{68} = 0.0204 \text{ min}^{-1}$$

$$\text{Also,} \quad t_{\frac{1}{2}} = \frac{0.693}{\lambda} = \frac{0.693}{0.0204} = 34 \text{ min.}$$

Example 11.5. One gram of a radioactive element decays by β-emission to 0.125 g in 200 hours. How much more time will elapse until only 0.10 gram of it is left?

Solution. We know, $\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$

Given: $N_0 = 1$; $N = 0.125$; $t = 200$ hr

Thus: $\lambda = \frac{2.303}{200} \log \frac{1}{0.125} = \frac{2.303}{200} \times 0.9031 = 0.0104 \text{ hr}^{-1}$.

To calculate the time t that will elapse when 0.125 g ($= N_0$) of the element decays to 0.10 g ($= N$), substitute these values and the value of λ in the equation:

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N} = \frac{2.303}{0.0104} \log \frac{0.125}{0.10} = 21.46 \text{ hr.}$$

11.9. CARBON DATING

Willard Libby has shown that by measuring the radioactivity of ${}^{14}_{6}C$ (usually called carbon-14 or C-14), it is possible to determine the date at which a plant was cut or animal died. He was awarded Nobel Prize for his work in developing this method known as *carbon dating*.

The principle of the method is that radioactive ${}^{14}_{6}C$ is produced in the upper atmosphere according to the reaction:

$${}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

The neutrons required in the reaction are formed by cosmic rays. There is one atom of ${}^{14}_{6}C$ for every 7.49×10^{11} C atoms in the carbon dioxide of the atmosphere and in all living animals and plants. The proportion does not change with time because as fast as ${}^{14}_{6}C$ nuclei are destroyed by radioactive decay (half-life period of ${}^{14}_{6}C$ = 5760 years), they are replenished by the bombardment of cosmic ray neutrons on nitrogen. The radioactive carbon produced in this way becomes part of a carbon dioxide molecule and is subsequently consumed by the plants and through them by animals. It means that any sample of carbon derived from living plants or animals or from the atmosphere will have the same rate of decay—15 3 disintegrations (β-particles) per minute per gram of carbon. However, when plants are cut or the animals die, they are removed from the carbon cycle and the ${}^{14}_{6}C$ starts disintegrating according to the reaction :

$$ {}^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e $$

Thus by measuring the radioactivity and knowing the $t_{\frac{1}{2}}$ of ${}^{14}_{6}C$, it is possible to know when the sample was removed from the carbon cycle. The method is illustrated in Fig. 11.7 and is frequently employed in geological and archaeological dating of the ancient samples.

Example 11.6. A wooden article found in a cave has only 40% as much C-14 activity as a fresh piece of wood. How old is the article ($t_{\frac{1}{2}}$ for C-14=5760 years)?

Solution. $N_0=100\%$, $N=40\%$ of N_0, $t_{\frac{1}{2}}=5760$

$$ \text{We know, } t_{\frac{1}{2}}=\frac{0.693}{\lambda}=5760 \text{ years} $$

$$ \text{Therefore, } \lambda=\frac{0\ 693}{5760}=1.203\times10^{-4}\ \text{year}^{-1} $$

Substituting these values in the equation:

$$ t=\frac{2.303}{\lambda}\log\frac{N_0}{N} $$

$$ =\frac{2.303}{1.203\times10^{-4}}\log\frac{100}{40} $$

$$ =7.617\times10^{3}\ \text{years.} $$

Example 11.7. A sample of carbon derived from one of the Dead Sea scrolls is found to be decaying at the rate of 12.0 disintegrations per unit per gram of carbon. Estimate the age of the Dead Sea scrolls (carbon from living plants disintegrates at the rate of 15.3 disintegrations per minute per gram).

Solution. We know, $t_{\frac{1}{2}}=\frac{0.693}{\lambda}=5760$ years

$$ \text{Therefore, } \lambda=\frac{0.693}{5760}=1.203\times10^{-4}\ \text{year}^{-1} $$

$$\text{Now, } t = \frac{2303}{1.203 \times 10^{-4}} \log \frac{15.3}{12.0}$$

$$= 2.02 \times 10^{3} \text{ years.}$$

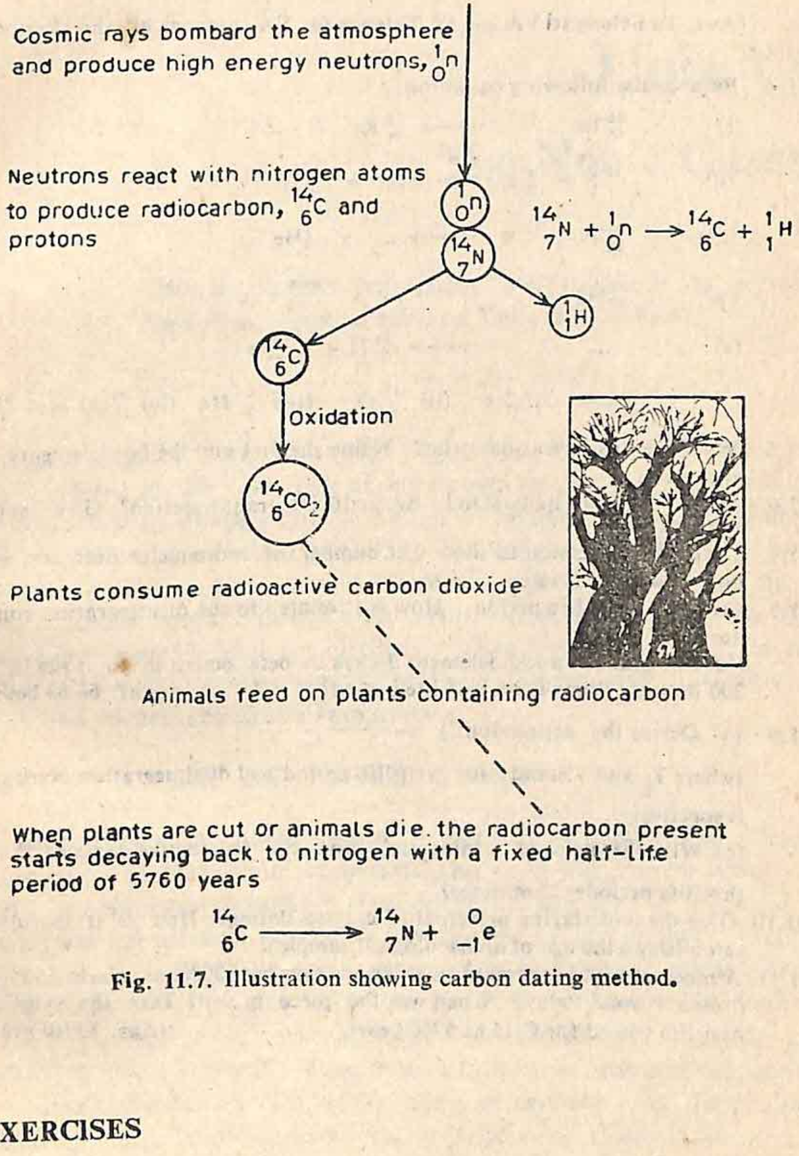

Cosmic rays bombard the atmosphere and produce high energy neutrons, $^{1}_{0}n$
Neutrons react with nitrogen atoms to produce radiocarbon, $^{14}_{6}C$ and protons
$^{1}_{0}n$
$^{14}_{7}N$
$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$
$^{1}_{1}H$
$^{14}_{6}C$
Oxidation
$^{14}_{6}CO_2$
Plants consume radioactive carbon dioxide
Animals feed on plants containing radiocarbon
When plants are cut or animals die. the radiocarbon present starts decaying back to nitrogen with a fixed half-life period of 5760 years
$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e$

Fig. 11.7. Illustration showing carbon dating method.

EXERCISES

11.1 (a) Give a brief account of radioactivity.

(b) Describe the characteristics of α-, β- and γ-rays.

11.2 What are the types of radiations given off by radioactive substances? Arrange the radiations in order of their penetrating power.

11.3 (a) State and explain the group displacement law.

(b) From the following nuclear reaction, predict the position of the two elements:

$$^{186}_{73}\text{Ta} \longrightarrow\ ^{186}_{74}\text{W} +\ ^{0}_{-1}\text{e}$$

(Ans. Ta belong to VA and W belongs to VA groups of the Periodic Table)

11.4 Balance the following equations:

(i) $^{82}_{35}\text{Br} \longrightarrow\ ^{82}_{36}\text{Kr} + \ldots$

(ii) $^{14}_{7}\text{N} +\ ^{4}_{2}\text{He} \longrightarrow \ldots +\ ^{1}_{1}\text{H}$

(iii) $^{210}_{84}\text{Po} \longrightarrow \ldots +\ ^{4}_{2}\text{He}$

(v) $^{27}_{12}\text{Mg} \longrightarrow \ldots +\ ^{0}_{-1}\text{e}$

(v) $\ldots \longrightarrow\ ^{14}_{7}\text{H} +\ ^{0}_{-1}\text{e}$

(Ans. (i) $^{0}_{-1}$e (ii) $^{17}_{8}$O (iii) $^{4}_{2}$He (iv) $^{27}_{13}$Al (v) $^{14}_{6}$C)

11.5 What are disintegration series? Name the first and the last elements in each case.

11.6 What do you understand by artificial transmutation? Give some examples.

11.7 Derive an expression to show that number of radionuclei decreases exponentially with time.

11.8 (a) Define half-life period. How is it related to the disintegration constant?

(b) One gram of a radioelement decays by beta emission to 0.125 g in 200 hours. What is its half-life period? **(Ans. 66.53 hours)**

11.9 (a) Derive the expression: $t_{\frac{1}{2}} = \dfrac{0.693}{\lambda}$

(where $t_{\frac{1}{2}}$ and λ stand for half-life period and distintegration constant, respectively).

(b) With the help of a diagram, show the radioactive decay of $^{128}_{53}$I (halflife period = 25 minutes).

11.10 Give the underlaying principal of carbon dating. How is it useful in establishing the age of archaeological samples?

11.11 A piece of wood recovered in an excavation has 30% as much C-14 as ordinary wood today. When was the piece buried? Take the value of half-life period for C-14 as 5760 years. **(Ans. 10010 years)**

Unit 12

The Noble Gases

Discovery, electronic structure, trends in properties and uses. Preparation of XeF_2 *and* XeF_4.

The gases helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) are collectively known as *zero group* (or *helium group*) elements of the Periodic Table. The gases occur in atmosphere (argon to an extent of 0.93% by volume, Table 12.1) and thus the name *rare gases* does not seem appropriate. They enter into chemical combinations under certain conditions and hence the name *inert gases* is also not justified. They are better called *noble gases* (like noble metals) because of their comparative unreactivity and also occurrence in the free state.

12.1. DISCOVERY OF NOBLE GASES

In 1785, Henry Cavendish passed repeated electric sparks in a mixture of dry air (free from carbon dioxide) and oxygen in order to achieve complete conversion of nitrogen of the air to its oxides. The resulting nitrogen oxides were absorbed in caustic potash solution and the excess oxygen was removed by potassium pentasulphide. Still a very small volume of the gas (1/120th of the original volume of air) was left behind which neither combined with oxygen nor with any other element. This remarkable observation of Cavendish remained unnoticed for more than a century. In 1895, Lord Rayleigh found that the density of nitrogen obtained from atmosphere was about 0.47% higher than that prepared from chemical sources such as by the decomposition of ammonium nitrite. He concluded that the nitrogen obtained from atmosphere contains some constituent or constituents which are heavier than nitrogen.

From spectroscopic studies, it was found to be a new gas and was given the name *argon* (from Greek word *argos*=inert or lazy). However, the new gas was soon found to be a mixture of a number of chemically inert gases and the spectrum originally indentified was also a mixed one. The brilliant researches of Rayleigh, Ramsay and Travers could lead to the discovery and isolation of all other nobel gases except radon from atmosphere. Radioactive and short-lived radon is identified in the decay series from uranium and thorium.

The history of discovery of helium is also very interesting. As early as 1868, Lockyer concluded that the bright yellow line (which he called D_3 line) observed in the solar spectrum during a total eclipse is due to the presence of a new element in the sun. He called this element *helium* (from the Greek word *helios*, the sun). Ramsay, in 1895, showed that the gas isolated by Hillebrand from uranium minerals had the same spectrum as helium discovered by Lockyer. Thus Ramsay was the first to characterize helium on the earth. In the same year, Kayser detected helium in the atmosphere.

12.2. GENERAL TRENDS

The electronic configurations and the general characteristics of the noble gases are summarized in Table 12.1 and Figs. 12.1-12.4. The typical element helium of the series has a saturated valence electron shell ($1s^2$) and all other gases have an octet of electrons in their outer shell. This imparts exceptional stability and consequently inactivity to the elements. The radii of the elements are very large (Fig. 12.1) and increase on descending the group as expected. These non-bonded radii should be compared with the van der Waals radii of the other elements and not with covalent bonded radii.

Table 12.1. Electronic Configurations and Some Properties of the Noble Gases

Noble gas	*Atomic number*	*Atomic weight*	*Electronic configuration*	*Abundance in atmosphere % volume*
He	2	4.003	$1s^2$	5.2×10^{-4}
Ne	10	20.179	[He] $2s^22p^6$	1.8×10^{-3}
Ar	18	39.948	[Ne] $3s^23p^6$	9.3×10^{-1}
Kr	36	83.30	[Ar] $3d^{10}4s^24p^6$	1.1×10^{-3}
Xe	54	131.30	[Kr] $4d^{10}5s^25p^6$	8.7×10^{-6}
Rn	86	222	[Xe] $4f^{14}5d^{10}6s^26p^6$	—

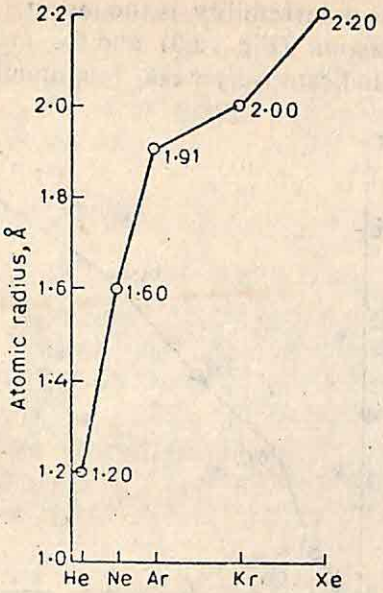


Fig. 12.1. Atomic radii of noble gases.

The ionization energies of the noble gases are of very high order (Fig. 12.2)—helium has the highest value (2372 kJ mol^{-1}) of all

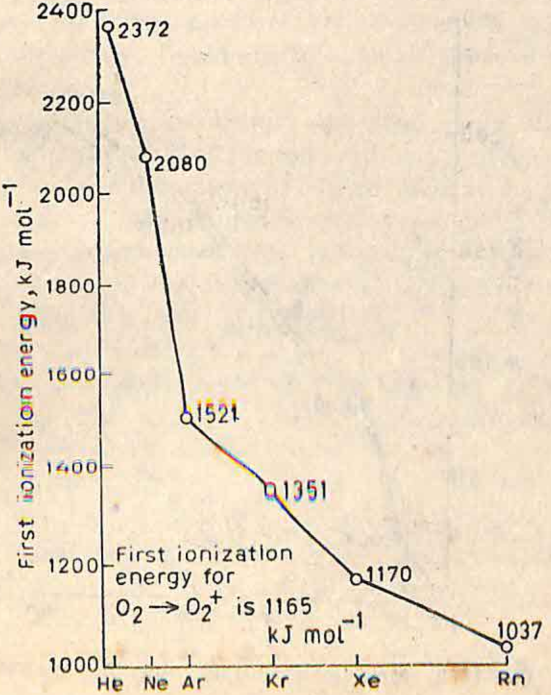


Fig. 12.2. Ionization energies of noble gases.

the elements and its polarizability is the lowest. Very low values for heat of vaporization (Fig. 12.3) and for melting and boiling points (Fig. 12.4) indicate very weak interatomic forces (van der

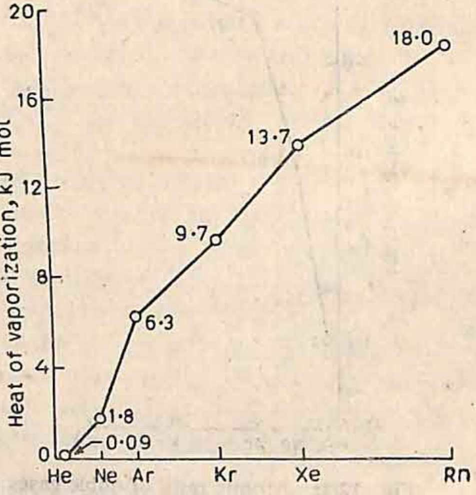


Fig. 12.3. Heats of vaporization of noble gases.

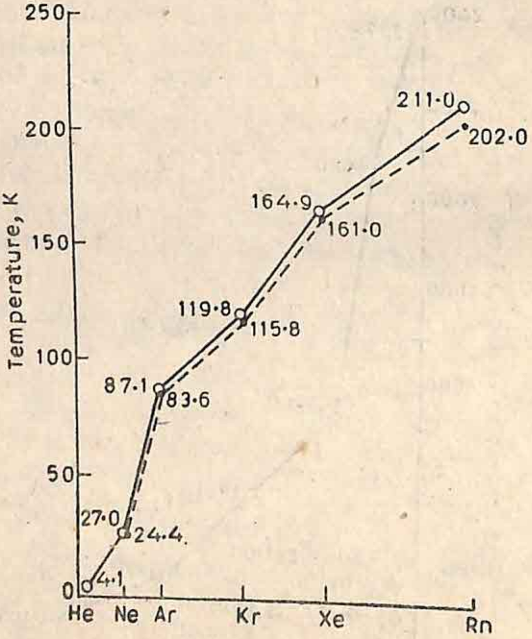


Fig. 12.4. Melting and boiling points of noble gases.

Waals type) between the monatomic elements. These forces arise because of the induction of a weak dipole in one electronic system by another. The increase in values (Figs. 12.3 and 12.4) with atomic weight points towards the increasing polarizability of the larger electronic clouds of the elements.

Special Properties of Helium

When helium is cooled below 2.178K at 1 atmospheric pressure, a remarkable liquid with abnormal properties is obtained. The liquid is referred to as *helium* II and the characteristic temperature is called the lambda (λ) point. The liquid is a superfluid, i.e., its viscosity is zero and it can flow up the surface of the vessel in which it is contained. It attains superconductivity, i.e., its electrical resistance is zero. It has anomalous values for specific heat, surface tension and compressibility.

12.3. ISOLATION

Because of the sufficient difference in boiling points, all the noble gases (except radon), nitrogen and oxygen can be obtained by the fractional distillation of liquid air (Fig. 12.5). As the boiling points of the noble gases increase from helium to xenon (Fig. 12.4), the gases escape from the liquid air in order of their volatility during the fractionation.

The boiling points of helium and neon are much lower than nitrogen, they escape liquefaction and accumulate over liquid nitrogen. The gaseous mixture of helium, neon and nitrogen passes through a spiral column cooled by liquid nitrogen, whereby most of the nitrogen gets liquified while helium and neon pass out. The residual nitrogen is completely removed by passing it over calcium carbide. The mixture of helium and neon is then cooled in liquid hydrogen when neon solidifies and helium passes on uncondensed.

There being a slight difference in the boiling points of oxygen and argon, the mixture of the two is circulated through a tube cooled by liquid nitrogen when oxygen condenses and argon passes out in the gaseous form.

The residual liquid becomes richer in krypton and xenon. It is fractionated by liquid air when the two are separated because of the considerable difference in their boiling points.

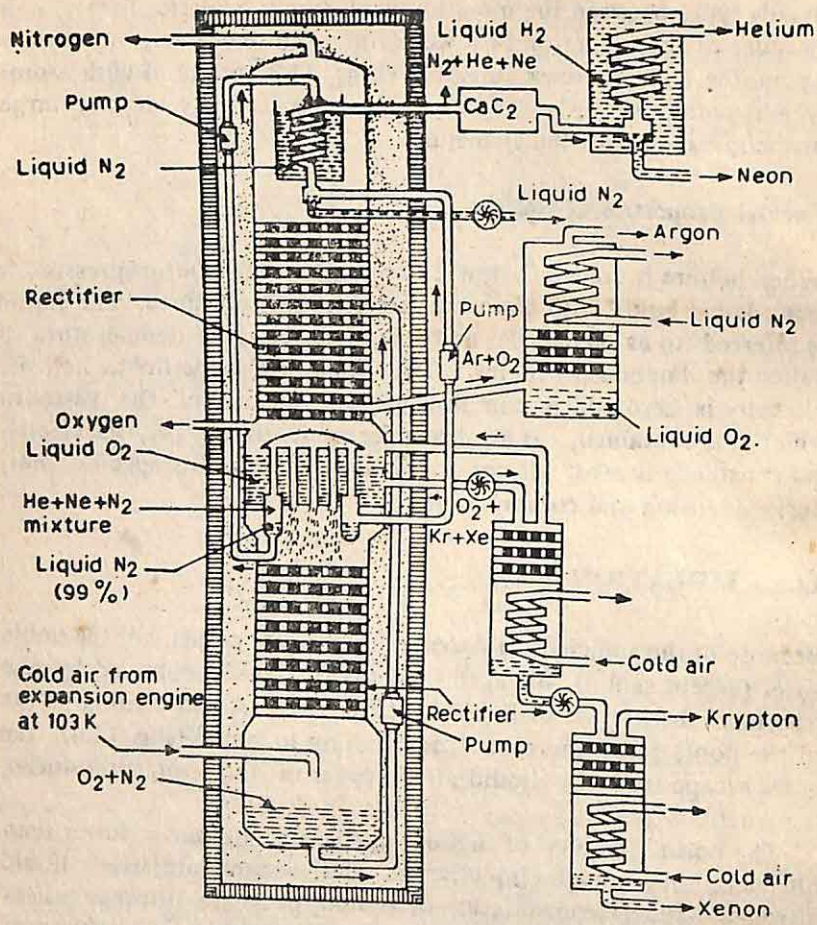


Fig. 12.5. Isolation of noble gases, nitrogen and oxygen by fractionation of liquid air.

12.4. USES

The noble gases are used for a variety of purposes. Some important uses of each one of them are given below.

Helium

(i) Being non-inflammable and very light, it finds extensive use in filling weather observation balloons and inflating aeroplane tyres.

(ii) A mixture of helium and oxygen is used by divers in preference to nitrogen-oxygen mixtures. Helium being much less soluble in blood than nitrogen, it does not cause pain (as it happens in case nitrogen is used) when a diver comes to the surface and the pressure is released.

(iii) Helium-oxygen mixture is also used in the treatment of asthama; the lightness and rapid diffusibility of helium reduces the muscular effort required in breathing.

(iv) Liquid helium is used to attain very low temperatures (in the neighbourhood of absolute zero) in scientific research. This has given birth to a new branch of science known as *cryogenics* under which we study the matter and its properties at very low temperature. The gas is also used in low temperature thermometry.

(v) Helium is used to provide inert atmosphere in the melting and welding of easily oxidizable metals and alloys.

(vi) Owing to its high viscosity, it is used as damper in compasses and other nautical instruments.

(vii) Being an inert gas, it is widely used in vacuum tubes, radio tubes, signal lamps and filling electrical transformers.

(viii) Helium is used in the fuel pressure systems for rockets and in heat transfer atmosphere for nuclear reactors.

(ix) A small amount of helium is sometimes added to neon lights to obtain a different colour.

Neon

(i) When neon is subjected to an electric discharge at a very low pressure (2 mm), it emits a characteristic orange-red glow. Besides being attractive, this glow is visible even in mists and fogs. Thus, *neon lights* are used for advertising purposes and as *beacon lights* for pilots. Different shades are obtained by varying the colour of the tube and using a suitable mixture of neon with mercury vapours or other noble gas. Neon is also used in photography.

(ii) Neon-helium mixtures do not conduct electricity until a certain limiting voltage is reached. Only after this point, they become conductors. This property is used in safety devices for protecting electrical instruments from high voltages.

(iii) Neon light is used in botanical gardens as it stimulates growth and helps the formation of chlorophyll.

Argon

(i) It is mainly used in filling incandescent lamps where it checks the volatilization of the tungsten filament and enhances its life.

(ii) It is also used for blending neon in discharge tubes to obtain different colours for illuminatio

(iii) It provides inert atmosphere in welding and in metallurgical operations.

Krypton and Xenon

These gases are also used in incandescent, fluorescent and discharge lamps. It has been found that they are superior to argon for filling the electric bulbs.

Krypton is used in ionization chamber for cosmic ray measurements. Xenon is used in the construction of xenon bubble chamber for the detection of uncharged radiations.

Radon

It is used in the treatment of cancer (radiotherapy) and in radioactive research.

12.5. NOBLE GAS COMPOUNDS

No real compounds of the noble gases were known before 1962. As the highly oxidizing PtF_6 could oxidize oxygen

$$PtF_6 + O_2 \longrightarrow O_2^+[PtF_6]^-$$

it was thought that xenon should also react in the same way. This is because the first ionization energy for the reaction $Xe \rightarrow Xe^+$ is nearly the same as that of $O_2 \rightarrow O_2^+$ (Fig. 12.2). In June 1962, N. Bartlett could actually prepare yellow-red powder corresponding to $Xe^+PtF_6^-$ by interaction of PtF_6 with xenon.

$$Xe + PtF_6 \xrightarrow{298K} Xe^+PtF_6^-$$

This was the beginning of the research in very interesting field of noble gas compounds. Since then many compounds have been isolated and characterized. Some more important xenon fluorides are decribed below:

Xenon Fluorides

XeF_2, XeF_4 or XeF_6 is obtained by the interaction of xenon with fluorine. The product obtained depends on the temperature, pressure and mixing ratio of the constituents. Thus,

$$\underset{(2:1 \text{ ratio})}{Xe + F_2} \xrightarrow{675K,\ 2\ hr} XeF_2$$

$$\underset{(1:5\ \text{ratio})}{Xe + 2F_2} \xrightarrow{725\text{-}735K} XeF_4$$

$$\underset{(1:20\ \text{ratio})}{Xe + 3F_2} \xrightarrow[50\ \text{atm}]{575K,\ 10\text{-}20\ \text{hr},} XeF_6$$

It can be seen from the following pressure versus temperature diagrams of xenon fluorides (Figs. 12.6 and 12.7) that XeF_4 will always be contaminated with some amounts of lower (i.e., XeF_2) and higher (i.e., XeF_6) fluorides. It can be purified by making use of its inability to donate fluoride ion to AsF_5 acceptor. Impure XeF_4 is dissolved in BrF_5 and treated with an excess of AsF_5. XeF_2 and XeF_6 from involatile salts while unreacted BrF_5 and AsF_5 are distilled off at 273K. The unchanged pure XeF_4 is then obtained by vacuum distillation at room temperature.

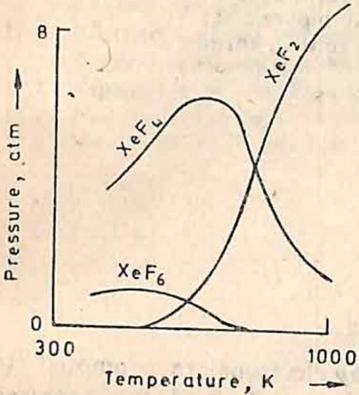


Fig. 12.6. Pressure *vs.* temperature diagram of xenon fluorides (Xe-Fe$_2$ ratio, 1 : 3).

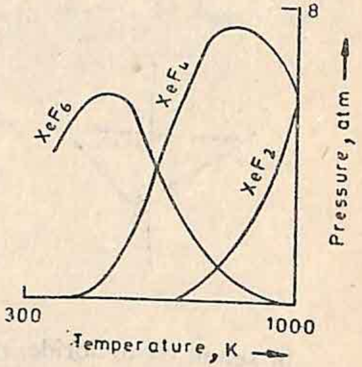


Fig. 12.7. Pressure *vs.* temperature diagram of xenon fluorides (Xe-F_2 ratio, 1 : 10).

Xenon hexafluoride can also be further purified by taking advantage of its ability to form stable complex with sodium fluoride. The likely impurities of other fluorides do not react with sodium fluoride and are pumped off at 325K. The stable $2NaF.XeF_6$ is then heated to 400K under vacuum when it gives pure XeF_6.

12.6. STRUCTURES OF XENON FLUORIDES

Xenon fluorides are formed by covalent bonding. In the formation of XeF_2, one of the 5*p* electrons in xenon is unpaired and promoted to the 5*d* orbital. The two unpaired electrons form bonds with two fluorine atoms. This is a case of sp^3d hybridization. The molecule possesses a trigonal bipyramidal structure. The xenon and fluorine atoms lie in a straight line (linear position) while the three lone pairs occupy the equitorial positions.

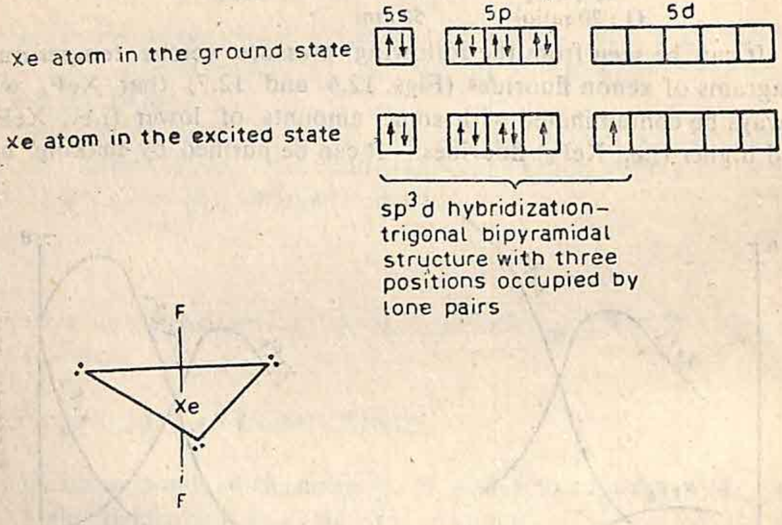


Fig. 12.8.

In xenon tetrafluoride, two of the $5p$ electrons are promoted to the $5d$ orbitals. Two unpaired electron in $5p$ and two unpaired electrons in $5d$ (total 4 unpaired electrons) form bonds with 4 fluorine

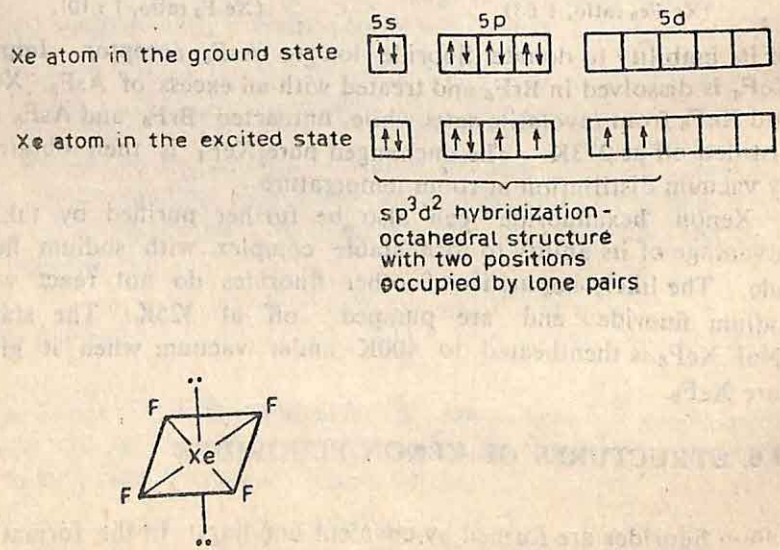

5s
5p
5d
Xe atom in the ground state
Xe atom in the excited state
sp^{3}d^2 hybridization -
octahedral structure
with two positions
occupied by lone pairs
F
F
Xe
F
F

Fig. 12.9.

atoms. This is a case of sp^3d^2 hybridization and gives rise to octahedral structure for the molecule. Because of the presence of two lone pairs. the geometry is distorted and the molecule acquires a square planar structure.

EXERCISES

12.1 What are the noble gases? Give a brief account of the history of their discovery.

12.2 Give the electronic configurations of the noble gases and discuss their general characteristics.

12.3 What is helium II? How is it prepared? Give its special characteristics.

12.4 Briefly describe the isolation of noble gases from liquid air.

12.5 Arrange the noble gases in order of their increasing atomic number and give their chief uses.

12.6 What are the various names given to the elements of the zero group of the Periodic Table? Justify the name 'noble gases' for them.

12.7 Explain the reaction between xenon and platinum hexafluoride.

12.8 How are xenon fluorides prepared?

12.9 Discuss the structure of XeF_2 and XeF_4.

Unit 13

Metallurgical Operations

Rocks, minerals and chief ores. General methods of beneficiation of ores. Extraction and refining of metals with specific examples.

Most metals occur in the combined state. Only metals which are very unreactive such as platinum, gold, etc., occur in the *free state* or *native form*. The compounds of metals which occur in the earth's crust are called *minerals*. The minerals are usually associated with rocky and earthy impurities called *gangue*. Those naturally occurring minerals which can be used for profitable extraction of metals are called *ores*.

13.1. OCCURRENCE OF METALS

It has been said that most metals occur in the combined form and only very unreactive metals occur in the elemetary form. It may be noted that majority of the metals are derived from the oxide ores or metal oxides obtained from carbonate or sulphide ores. The main types of ores with appropriate examples are given in Table 13.1.

Mixtures of minerals that make up the earth's crust are called *rocks*. These rocks are of three types:

(i) Igneous Rocks

In these rocks, the minerals were formed by direct cooling of the molten material of the earth. They contain mica, felspar, quartz, etc.

(ii) Sedimentary Rocks

These contain minerals which were formed by subsequent changes in the rocks. They include salt deposits, silicious matter, lime stone, dolomite, etc.

TABLE 13.1: Natural Occurrence of Metals

Type of ore	*Examples*
Native form	Cu, Ag, Au, Pd, Pt
Oxides	$Al_2O_3.2H_2O$ (Bauxite): SnO_2 (Tin stone or cassiterite): TiO_2 (Rutile); $FeO.TiO_2$ (Ilmenite); $FeO.Cr_2O_3$ (Chromite); MnO_2 (Pyrolusite); Fe_2O_3 (Haematite); Fe_3O_4 (Magnetite); ZnO (Zincite)
Carbonates	$MgCO_3$ (Magnesite); $CaCO_3.MgCO_3$ (Dolomite); $CaCO_3$ (Limestone); $SrCO_3$ (Strontianite); $BaCO_3$ (Witherite); $CuCO_3.Cu(OH)_2$ (Malachite); $ZnCO_3$ (Calamine)
Sulphides	PbS (Galena); Sb_2S_3 (Stibnite); Bi_2S_3 (Bismuth glance), NiS (Millerite); NiAsS (Nickel glance); Cu_2S (Copper glance); $Cu_2S.Fe_2S_3$ (Copper pyrites); Ag_2S (Silver glance); ZnS (Zinc blende); HgS (Cinnabar)
Halides	NaCl (Rock salt); KCl (Sylvine); $KCl.MgCl_2.6H_2O$ (Carnallite); AgCl (Horn silver)
Sulphates	$CaSO_4.2H_2O$ (Gypsum); $SrSO_4$ (Celestine), $BaSO_4$ (Barytes)
Silicates	$3BeO.Al_2O_3.6SiO_2$ (Beryl); $LiAl\ (SiO_3)_2$ (Spodumene); (Ni, Mg) $SiO_3.nH_2O$ (Garnierite)
Phosphates	$LiF.AlPO_4$ (Amblygonite); $(Li, Na)PO_4.(Fe, Mn)_3\ (PO_4)_2$ (Triphylite)

(iii) Metamorphic Rocks

In these rocks, the minerals have undergone change in their composition and crystalline form because of extreme temperatures and pressures. They include kaynite, garnet, etc.

13.2. METALLURGY

The process of extracting metals from their ores is called *metallurgy*. It depends on the nature of the ore which is to be worked out for the metal. However, the various steps that are usually involved in the metallurgy are:

(i) Beneficiation, concentration or dressing of the ore.
(ii) Extraction of the metal from the concentrated ore.
(iii) Refining or purification of the impure metal.

Beneficiation of Ore

The ore is always associated with gangue. It is essential to remove these unwanted rocky and earth particles before proceeding for the

Unit 13

Metallurgical Operations

Rocks, minerals and chief ores. General methods of beneficiation of ores. Extraction and refining of metals with specific examples.

Most metals occur in the combined state. Only metals which are very unreactive such as platinum, gold, etc., occur in the *free state* or *native form*. The compounds of metals which occur in the earth's crust are called *minerals*. The minerals are usually associated with rocky and earthy impurities called *gangue*. Those naturally occurring minerals which can be used for profitable extraction of metals are called *ores*.

13.1. OCCURRENCE OF METALS

It has been said that most metals occur in the combined form and only very unreactive metals occur in the elemetary form. It may be noted that majority of the metals are derived from the oxide ores or metal oxides obtained from carbonate or sulphide ores. The main types of ores with appropriate examples are given in Table 13.1.

Mixtures of minerals that make up the earth's crust are called *rocks*. These rocks are of three types:

(i) Igneous Rocks

In these rocks, the minerals were formed by direct cooling of the molten material of the earth. They contain mica, felspar, quartz, etc.

(ii) Sedimentary Rocks

These contain minerals which were formed by subsequent changes in the rocks. They include salt deposits, silicious matter, lime stone, dolomite, etc.

TABLE 13.1: Natural Occurrence of Metals

Type of ore	*Examples*
Native form	Cu, Ag, Au, Pd, Pt
Oxides	$Al_2O_3.2H_2O$ (Bauxite): SnO_2 (Tin stone or cassiterite): TiO_2 (Rutile); $FeO.TiO_2$ (Ilmenite); $FeO.Cr_2O_3$ (Chromite); MnO_2 (Pyrolusite); Fe_2O_3 (Haematite); Fe_3O_4 (Magnetite); ZnO (Zincite)
Carbonates	$MgCO_3$ (Magnesite); $CaCO_3.MgCO_3$ (Dolomite); $CaCO_3$ (Limestone); $SrCO_3$ (Strontianite); $BaCO_3$ (Witherite); $CuCO_3.Cu(OH)_2$ (Malachite); $ZnCO_3$ (Calamine)
Sulphides	PbS (Galena); Sb_2S_3 (Stibnite); Bi_2S_3 (Bismuth glance), NiS (Millerite); NiAsS (Nickel glance); Cu_2S (Copper glance); $Cu_2S.Fe_2S_3$ (Copper pyrites); Ag_2S (Silver glance); ZnS (Zinc blende); HgS (Cinnabar)
Halides	NaCl (Rock salt); KCl (Sylvine); $KCl.MgCl_2.6H_2O$ (Carnallite); AgCl (Horn silver)
Sulphates	$CaSO_4.2H_2O$ (Gypsum); $SrSO_4$ (Celestine), $BaSO_4$ (Barytes)
Silicates	$3BeO.Al_2O_3.6SiO_2$ (Beryl); $LiAl\,(SiO_3)_2$ (Spodumene); $(Ni, Mg)\,SiO_2.nH_2O$ (Garnierite)
Phosphates	$LiF.AlPO_4$ (Amblygonite); $(Li, Na)PO_4.(Fe, Mn)_3\,(PO_4)_2$ (Triphylite)

(iii) Metamorphic Rocks

In these rocks, the minerals have undergone change in their composition and crystalline form because of extreme temperatures and pressures. They include kaynite, garnet, etc.

13.2. METALLURGY

The process of extracting metals from their ores is called *metallurgy*. It depends on the nature of the ore which is to be worked out for the metal. However, the various steps that are usually involved in the metallurgy are:

(i) Beneficiation, concentration or dressing of the ore.
(ii) Extraction of the metal from the concentrated ore.
(iii) Refining or purification of the impure metal.

Beneficiation of Ore

The ore is always associated with gangue. It is essential to remove these unwanted rocky and earth particles before proceeding for the actual extraction of the metal. The process of removing these undesirable impurities is called *beneficiation*, *concentration* or *dressing* of the ore. This may be achieved by one or more of the following methods:

(i) HAND PICKING

In this preliminary method, the ore is separated by hand picking and the adherent gangue is broken away with a hammer.

(ii) LEVIGATION OR WASHING WITH WATER

In this method, the crushed ore is washed with a stream of water when the lighter gangue particles are washed away while the heavier ore particles are left behind (Fig. 13.1).

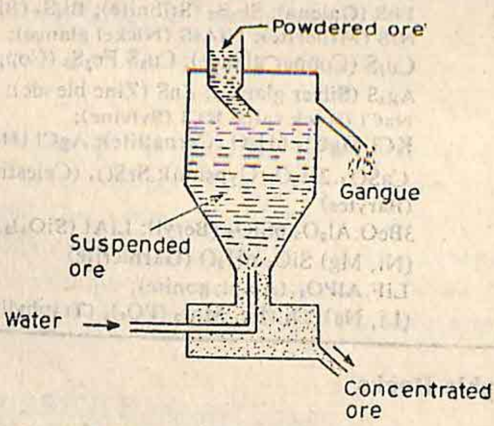


Fig. 13.1. Levigation or washing with water.

(iii) FROTH FLOTATION PROCESS

This method is used for the concentration of sulphide ores like PbS (galena), ZnS (zinc blende), etc. It is based on the principle that the gangue particles are preferentially wetted by water while the ore particles by oil.

The crushed and finely powdered ore is treated with water and pine oil in a tank. It is then agitated violently with water when a froth is formed. This froth carries away along with it the ore particles to the surface while gangue is left behind

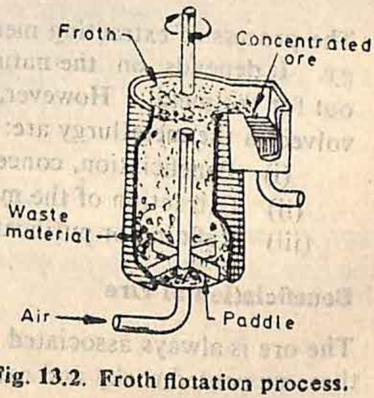


Fig. 13.2. Froth flotation process.

(Fig. 13.2). The foam is then washed with water to recover the ore in the concentrated form.

(iv) MAGNETIC SEPARATION

Ferromagnetic ores, such as Fe_3O_4, are separated from non-magnetic gangue using magnetic separators. The separator consists of a leather belt moving over two rollers, one of which is magnetic. When the ore is dropped on one end of the belt, it is separated into two heaps—magnetic and non-magnetic—at the other end of the belt. It is because the magnetic ore is attracted by the magnetic roller and falls nearer to it while the non-magnetic gangue is thrown further apart and forms a separate heap (Fig. 13.3).

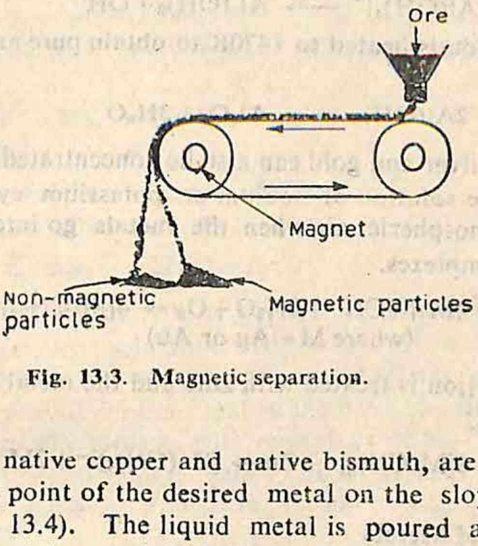


Fig. 13.3. Magnetic separation.

(v) LIQUATION

The ores, such as native copper and native bismuth, are heated just above the melting point of the desired metal on the sloping hearth of a furnace (Fig. 13.4). The liquid metal is poured away while the infusible impurities are left behind. This process, known as ***liquation***, is applied to concentrate ores having melting points lower than the impurities.

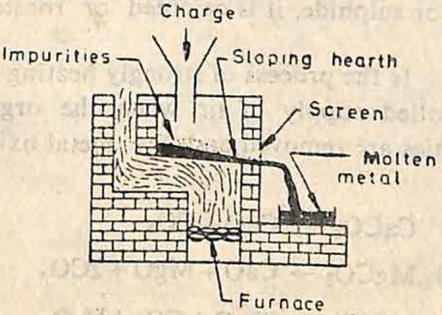


Fig. 13.4. Liquation.

(vi) LEACHING

In this process, the powdered ore is treated with a suitable reagent which dissolves the ore but not the impurities. The bauxite ore ($Al_2O_3.2H_2O$) contains the main impurities of iron oxide and silicates. When it is treated with hot sodium hydroxide solution, Al_2O_3 dissolves but the impurities are left behind and filtered off.

$$Al_2O_3+2OH^-+3H_2O \longrightarrow \underset{\text{Soluble aluminate}}{2[Al(OH)_4]^-}$$

The filtrate is seeded with a little freshly precipitated aluminium hydroxide when most of the metal from the solution is precipitated as hydroxide.

$$[Al(OH)_4]^- \longrightarrow Al\,(OH)_3+OH^-$$

The hydroxide is heated to 1470K to obtain pure anhydrous alumina Al_2O_3.

$$2Al(OH)_3 \longrightarrow Al_2O_3+3H_2O$$

Native silver and gold can also be concentrated by leaching them with a dilute solution of sodium or potassium cyanide in the presence of atmospheric air when the metals go into solution in the form of complexes.

$$4M+8CN^-+2H_2O+O_2 \rightarrow 4[M(CN)_2]^-+4OH^-$$
$$\text{(where } M=Ag \text{ or } Au)$$

The solution is treated with zinc and the metal silver or gold is precipitated.

$$2[M(CN)_2]^-+Zn \rightarrow [Zn(CN)_4]^{2-}+2M$$

Extraction of Metals

After concentration, the ore is worked out for extraction of the metal. In case the ore consists of a carbonate, hydroxide, hydrated oxide or sulphide, it is calcined or roasted to the oxide form.

Calcination. Is the process of strongly heating the concentrated ore in a controlled supply of air when the organic matter and volatile impurities are removed and the metal oxides are obtained. For example :

$$CaCO_3 \rightarrow CaO+CO_2$$

$$CaCO_3.MgCO_3 \rightarrow CaO+MgO+2CO_2$$

$$CuCO_3.Cu(OH)_2 \rightarrow 2CuO+CO_2+H_2O$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$
$$Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O$$
$$2Fe_2O_3.3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$$

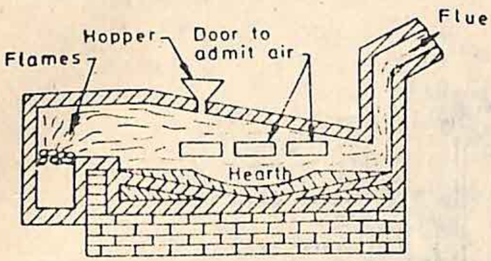


Fig. 13.5. A reverberatory furnace.

Calcination is usually carried out in a reverberatory furnace (Fig. 13.5). The term *roasting* is more widely applied to represent the process in which an ore (usually the sulphide ore) is heated in the presence of air at a temperature below its melting point when the metal is converted to its oxide or sulphate. For example:

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$CuS + 2O_2 \rightarrow CuSO_4$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The calcined or roasted ore is reduced to the metallic form. The high-temperature reduction process in which the metal is usually obtained in a molten state is called *smelting*. The smelting operations are usually carried out in the presence of a *flux*. The flux is a substance which reacts with impurities of the ore to form fusible silicate or phosphate called *slag*. If the ore contains acidic impurities like SiO_2, P_4O_{10}, etc., a basic flux such as CaO or $MgCO_3$ is used.

$$\underset{\text{(Acidic impurity)}}{SiO_2} + \underset{\text{(Basic flux)}}{CaO} \rightarrow \underset{\text{(Slag)}}{CaSiO_3}$$
$$\underset{\text{(Acidic impurity)}}{P_4O_{10}} + \underset{\text{(Basic flux)}}{6CaO} \rightarrow \underset{\text{(Slag)}}{2Ca_3(PO_4)_2}$$

In case the impurities are of basic nature like CaO, MnO, FeO, etc., an acidic flux such as SiO_2 is used.

$$\underset{\text{(Basic impurity)}}{MnO} + \underset{\text{(Acidic flux)}}{SiO_2} \rightarrow \underset{\text{(Slag)}}{MnSiO_3}$$
$$\underset{\text{(Basic impurity)}}{FeO} + \underset{\text{(Acidic flux)}}{SiO_2} \rightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

(i) Reduction by Heating

Some metal oxides are thermally unstable. In such cases, the ore is directly reduced to the metallic form. For example, when

(vi) LEACHING

In this process, the powdered ore is treated with a suitable reagent which dissolves the ore but not the impurities. The bauxite ore ($Al_2O_3.2H_2O$) contains the main impurities of iron oxide and silicates. When it is treated with hot sodium hydroxide solution, Al_2O_3 dissolves but the impurities are left behind and filtered off.

$$Al_2O_3+2OH^-+3H_2O \longrightarrow \underset{\text{Soluble aluminate}}{2[Al(OH)_4]^-}$$

The filtrate is seeded with a little freshly precipitated aluminium hydroxide when most of the metal from the solution is precipitated as hydroxide.

$$[Al(OH)_4]^- \longrightarrow Al\,(OH)_3+OH^-$$

The hydroxide is heated to 1470K to obtain pure anhydrous alumina Al_2O_3.

$$2Al(OH)_3 \longrightarrow Al_2O_3+3H_2O$$

Native silver and gold can also be concentrated by leaching them with a dilute solution of sodium or potassium cyanide in the presence of atmospheric air when the metals go into solution in the form of complexes.

$$4M+8CN^-+2H_2O+O_2 \rightarrow 4[M(CN)_2]^-+4OH^-$$
$$\text{(where } M=Ag \text{ or } Au)$$

The solution is treated with zinc and the metal silver or gold is precipitated.

$$2[M(CN)_2]^-+Zn \rightarrow [Zn(CN)_4]^{2-}+2M$$

Extraction of Metals

After concentration, the ore is worked out for extraction of the metal. In case the ore consists of a carbonate, hydroxide, hydrated oxide or sulphide, it is calcined or roasted to the oxide form.

Calcination. Is the process of strongly heating the concentrated ore in a controlled supply of air when the organic matter and volatile impurities are removed and the metal oxides are obtained. For example :

$$CaCO_3 \rightarrow CaO+CO_2$$

$$CaCO_3.MgCO_3 \rightarrow CaO+MgO+2CO_2$$

$$CuCO_3.Cu(OH)_2 \rightarrow 2CuO+CO_2+H_2O$$

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$
$$Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O$$
$$2Fe_2O_3.3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$$

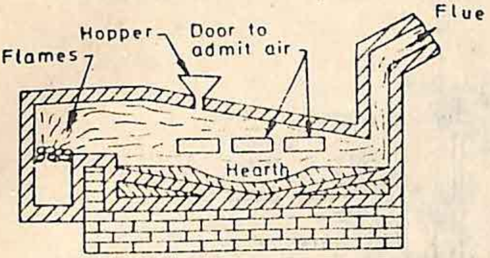


Fig. 13.5. A reverberatory furnace.

Calcination is usually carried out in a reverberatory furnace (Fig. 13.5). The term *roasting* is more widely applied to represent the process in which an ore (usually the sulphide ore) is heated in the presence of air at a temperature below its melting point when the metal is converted to its oxide or sulphate. For example:

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$CuS + 2O_2 \rightarrow CuSO_4$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

The calcined or roasted ore is reduced to the metallic form. The high-temperature reduction process in which the metal is usually obtained in a molten state is called *smelting*. The smelting operations are usually carried out in the presence of a ***flux***. The flux is a substance which reacts with impurities of the ore to form fusible silicate or phosphate called *slag*. If the ore contains acidic impurities like SiO_2, P_4O_{10}, etc., a basic flux such as CaO or $MgCO_3$ is used.

$$\underset{\text{(Acidic impurity)}}{SiO_2} + \underset{\text{(Basic flux)}}{CaO} \rightarrow \underset{\text{(Slag)}}{CaSiO_3}$$
$$\underset{\text{(Acidic impurity)}}{P_4O_{10}} + \underset{\text{(Basic flux)}}{6CaO} \rightarrow \underset{\text{(Slag)}}{2Ca_3(PO_4)_2}$$

In case the impurities are of basic nature like CaO, MnO, FeO, etc., an acidic flux such as SiO_2 is used.

$$\underset{\text{(Basic impurity)}}{MnO} + \underset{\text{(Acidic flux)}}{SiO_2} \rightarrow \underset{\text{(Slag)}}{MnSiO_3}$$
$$\underset{\text{(Basic impurity)}}{FeO} + \underset{\text{(Acidic flux)}}{SiO_2} \rightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

(i) Reduction by Heating

Some metal oxides are thermally unstable. In such cases, the ore is directly reduced to the metallic form. For example, when cinnabar, HgS (mixed with charcoal fuel), is heated in a shaft furnace (Fig. 13.6) it is reduced to mercury which is condensed.

$$\underset{\text{(Cinnabar)}}{HgS} + O_2 \rightarrow Hg + SO_2$$

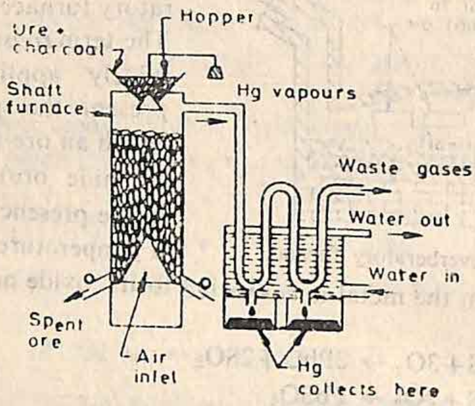


Fig. 13.6. Extraction of mercury using a shaft furnace.

(ii) Chemical Reduction

Several reducing agents such as carbon (in the form of charcoal, coke or coal), hydrogen, carbon monoxide and metals like sodium, magnesium and aluminium, are used for reduction. For example:

The concentrated cassiterite, SnO_2, is reduced to metallic tin by heating with coke at 1475-1575K in a reverberatory furnace or in a blast furnace.

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

Zinc blends,, ZnS, is concentrated by froth flotation process and is roasted to zinc oxide at about 1200K. The oxide is mixed with half of its weight of powdered coal or coke and heated in fire clay retorts (Fig. 13.7) to about 1700K. The metal distils off and condenses in the prolongs and earthenware condensers. It is a called *zinc spelter*.

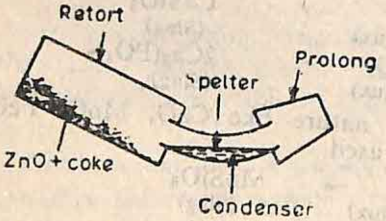


Fig. 13.7 Fire clay retort with a prolong used in the extraction of zinc.

The most important commercial metal, iron, is obtained by carbon reduction in a blast furnace (Fig. 13.8). The powdered haematite ore (Fe_2O_3) mixed with coke and limestone (flux) is fed into the top of the furnace and heated air (sometimes enriched with oxygen) is blown through tuyers near the bottom. The incoming air burns carbon to form carbon dioxide and large amount of heat is generated. The furnace attains the highest temperature (around 1775K) at this point.

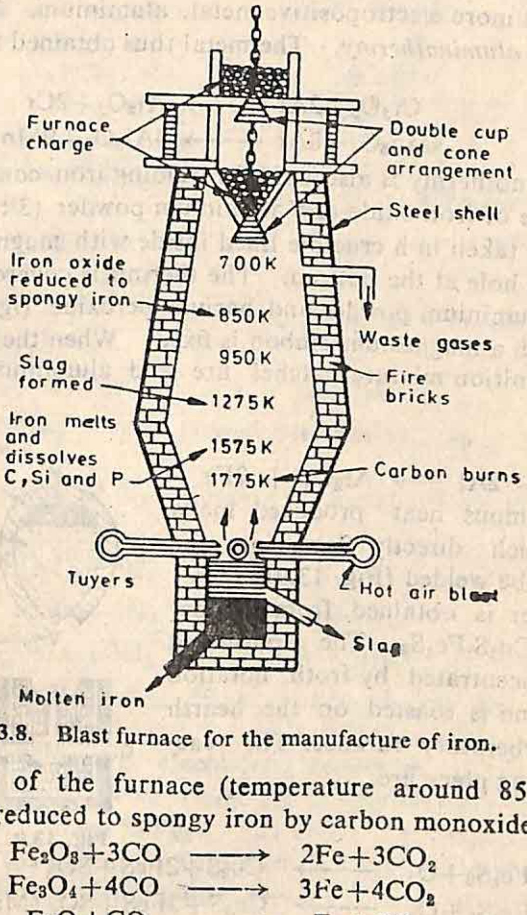


Fig. 13.8. Blast furnace for the manufacture of iron.

Near the top of the furnace (temperature around 850K), the iron oxides are reduced to spongy iron by carbon monoxide.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$
$$FeO + CO \longrightarrow Fe + CO_2$$

In the middle of the furnace (temperature around 1275K), slag is formed.

$$\underset{\text{(Limestone flux)}}{CaCO_3} \longrightarrow CaO + CO_2$$
$$CaO + \underset{\text{(Impurity)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

In the lower part of the furnace (temperature around 1575K), the spongy iron dissolves carbon, sulphur, phosphorus, manganese and silicon. The molten iron sinks at the bottom and forms a layer furnace (Fig. 13.6) it is reduced to mercury which is condensed.

$$\underset{\text{(Cinnabar)}}{HgS}+O_2 \rightarrow Hg+SO_2$$

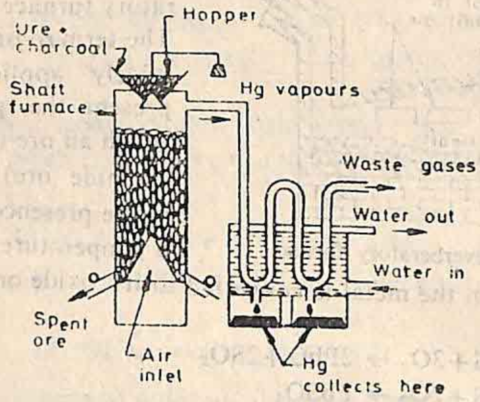


Fig. 13.6. Extraction of mercury using a shaft furnace.

(ii) Chemical Reduction

Several reducing agents such as carbon (in the form of charcoal, coke or coal), hydrogen, carbon monoxide and metals like sodium, magnesium and aluminium, are used for reduction. For example:

The concentrated cassiterite, SnO_2, is reduced to metallic tin by heating with coke at 1475-1575K in a reverberatory furnace or in a blast furnace.

$$SnO_2+2C \rightarrow Sn+2CO$$

Zinc blends,, ZnS, is concentrated by froth flotation process and is roasted to zinc oxide at about 1200K. The oxide is mixed with half of its weight of powdered coal or coke and heated in fire clay retorts (Fig. 13.7) to about 1700K. The metal distils off and condenses in the prolongs and earthenware condensers. It is a called *zinc spelter*.

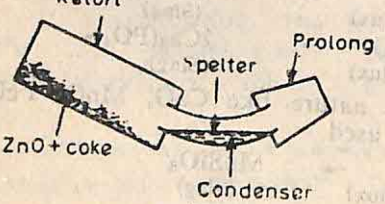


Fig. 13.7 Fire clay retort with a prolong used in the extraction of zinc.

The most important commercial metal, iron, is obtained by carbon reduction in a blast furnace (Fig. 13.8). The powdered haematite ore (Fe_2O_3) mixed with coke and limestone (flux) is fed into the top of the furnace and heated air (sometimes enriched with oxygen) is blown through tuyers near the bottom. The incoming air burns carbon to form carbon dioxide and large amount of heat is generated. The furnace attains the highest temperature (around 1775K) at this point.

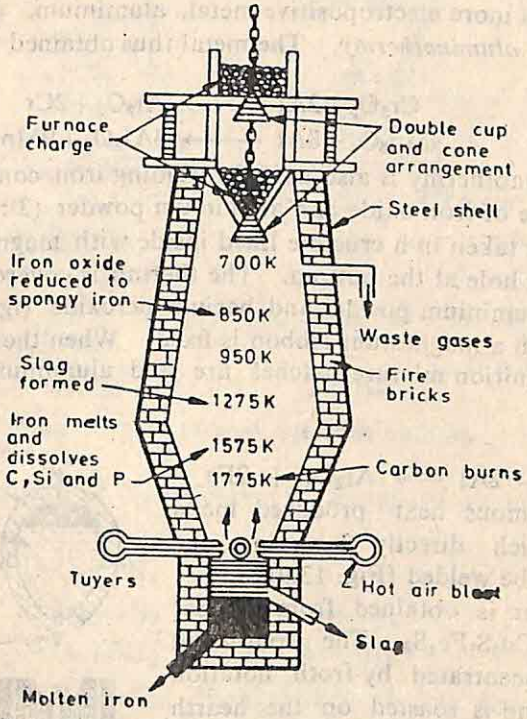


Fig. 13.8. Blast furnace for the manufacture of iron.

Near the top of the furnace (temperature around 850K), the iron oxides are reduced to spongy iron by carbon monoxide.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$
$$FeO + CO \longrightarrow Fe + CO_2$$

In the middle of the furnace (temperature around 1275K), slag is formed.

$$\underset{\text{(Limestone flux)}}{CaCO_3} \longrightarrow CaO + CO_2$$
$$CaO + \underset{\text{(Impurity)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

In the lower part of the furnace (temperature around 1575K), the spongy iron dissolves carbon, sulphur, phosphorus, manganese and silicon. The molten iron sinks at the bottom and forms a layer below the slag. It is removed periodically from a lower hole into sand moulds. It is called *cast iron* or *pig iron* and contains about 5% carbon.

The oxide of chromium or manganese is reduced to the metallic form by a more electropositive metal, aluminium. The process is known as *aluminothermy*. The metal thus obtained is in the molten state.

$$Cr_2O_3+2Al \longrightarrow Al_2O_3+2Cr$$
$$3Mn_3O_4+8Al \longrightarrow 4Al_2O_3+9Mn$$

Aluminothermy is also used for welding iron construction work. A mixture of iron oxide and aluminium powder (3 : 1 ratio) called *thermit* is taken in a crucible lined inside with magnesite and with a tapping hole at the bottom. The thermit is covered with a mixture of aluminium powder and barium peroxide (ignition mixture) into which a magnesium ribbon is fixed. When the ribbon is lighted, the ignition mixture catches fire and aluminium reduces iron oxide.

$$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$$

The enormous heat produced melts iron which directly flows into the crack to be welded (Fig. 13.9).

Copper is obtained from copper pyrites, $Cu_2S.Fe_2S_3$. The powdered ore is concentrated by froth flotation process and is roasted on the hearth of a reverberatory furnace. The reactions taking place are:

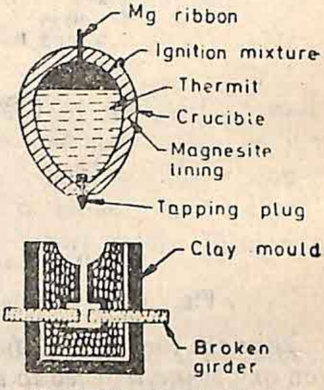


Fig. 13.9. Aluminothermy.

$$Cu_2S.Fe_2S_3+O_2 \longrightarrow Cu_2S+2FeS+SO_2$$
$$Cu_2S.Fe_2S_3+O_2 \longrightarrow Cu_2S+2FeS+SO_2 \text{ (Main reaction)}$$
$$\left.\begin{array}{l} 2Cu_2S+3O_2 \longrightarrow 2Cu_2O+2SO_2 \\ 2FeS+3O_2 \longrightarrow 2FeO+2SO_2 \end{array}\right. \text{(Minor reactions)}$$

The roasted ore is mixed with sand (flux) and a little coke and smelted in a blast furnace.

$$\underset{\text{(Flux)}}{FeO+SiO_2} \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$
$$Cu_2O+FeS \longrightarrow Cu_2S+FeO$$

The slag is removed and the molten mass containing mostly cuprous sulphide with a little ferrous sulphide forms the lower layer. This mixture of sulphides is called *matte*.

The molten matte is taken in a pear-shaped Bessemer converter (Fig. 13.10). A blast of air and sand is blown through tuyeres. Cuprous sulphide gets partially oxidized to cuprous oxide. The unchanged cuprous sulphide and the resulting cuprous oxide react to form copper.

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

It is called *blister copper* as it contains dissolved sulphur dioxide which imparts blister type appearance on the metal.

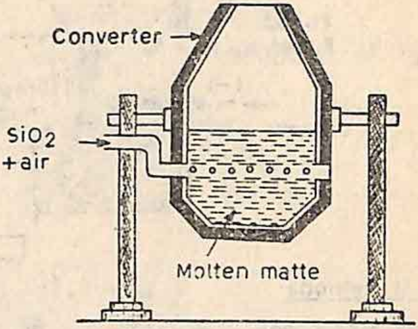


Fig. 13.10. Bessemer converter.

The metal titanium is obtained by reduction of its chloride with magnesium at 1075K in an inert atmosphere of argon.

$$TiCl_4 + 2Mg \longrightarrow Ti + 2MgCl_2$$

The reduction may also be carried out with sodium in the inert atmosphere.

Hydrogen is also used for reduction of metal oxides to metals. For example:

$$GeO_2 + 2H_2 \longrightarrow Ge + 2H_2O$$
$$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$$
$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

(iii) Electrolytic Reduction. Highly electropositive alkali and alkaline earth metals cannot be reduced by chemical reduction methods. These metals are obtained by electrolytic reduction of their fused chlorides. The electrolytic cells used for the preparation of sodium and magnesium are shown in Figs. 13.11 and 13.12, respectively.

Aluminium is also obtained by electrolytic reduction of alumina (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6) in a cell of the type shown in Fig. 13.13.

(iv) Special Techniques. Some metals are extracted by special techniques. For example, ores of silver and gold are leached with dilute cyanide solution when the metals form soluble complexes:

$$4M + 8CN^- + 2H_2O + O_2 \longrightarrow 4[M(CN)_2]^- + 4OH^-$$

(where M=Ag or Au)

The solution, when treated with more electropositive zinc, precipitates the metal silver or gold.

$$2[M(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2M$$

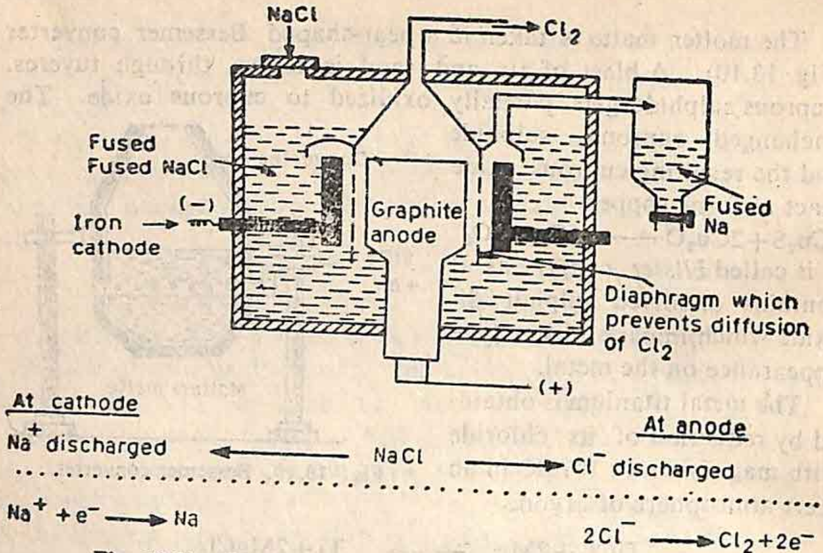


Fig. 13.11. Electrolytic cell for the production of sodium.

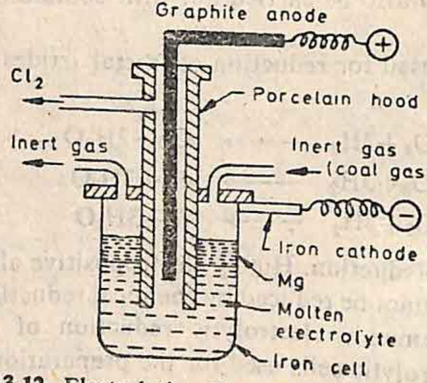
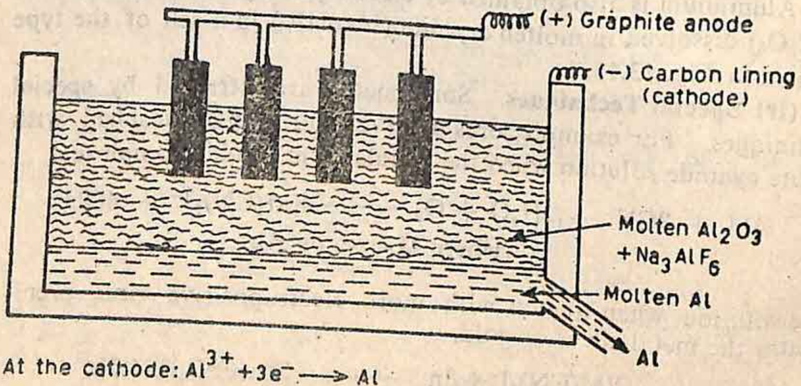


Fig. 13.12. Electrolytic cell for the production of magnesium.


(+) Graphite anode
(−) Carbon lining (cathode)
Molten Al$_2$O$_3$ + Na$_3$AlF$_6$
Molten Al
Al

At the cathode: $Al^{3+} + 3e^- \longrightarrow Al$

At the anode: $C(s) + 2O^{2-} \longrightarrow CO_2(g) + 4e^-$

Low grade copper ores are converted to copper sulphate by exposing them to air and water. The metal copper is then precipitated by adding more electropositive scrap iron to the copper solution.

$$CuSO_4 + Fe \longrightarrow FeSO_4 + Cu$$

Metal-extraction techniques of some metals are summarized in Table 13.2.

TABLE 13.2: Metal Extraction Techniques

Metal	*Reduction electrode potential (V)*	*Chief ore*	*Main method of extraction*	*Equation for extraction*
Li	−3.05	$LiAl(SiO_3)_2$ (Spodumene)	Electrolysis of fused LiCl containing KCl	Electrolytic reduction in each case $M^{n+} + ne^- \longrightarrow M$
K	−2.93	$KCl.MgCl_2.6H_2O$ (Carnallite)	Electrolysis of fused KCl containing $CaCl_2$	
Ba	−2.90	$BaCO_3$ (Witherite) $BaSO_4$ (Barytes)	Electrolysis of fused $BaCl_2$	
Sr	−2.89	$SrCO_3$ (Strontianite) $SrSO_4$ (Celestine)	Electrolysis of fused $SrCl_2$	
Ca	−2.76	$CaCO_3$ (Limestone) $CaSO_4$ (Gypsum)	Electrolysis of fused mixture of $CaCl_2$ and CaF_2	
Na	−2.71	NaCl (Rock salt)	Electrolysis of fused NaCl containing $CaCl_2$	
Mg	−2.38	$KCl.MgCl_2.6H_2O$ (Carnallite $MgCO_3$ (Magnesite)	Electrolysis of fused $MgCl_2$ containing KCl	
Be	−1.70	$3BeO.Al_2O_3.6SiO_2$ (Beryl)	Electrolysis of fused BeF_2 containing NaF	
Al	−1.66	$Al_2O_3.2H_2O$ (Bauxite)	Electrolysis of Al_2O_3 in molten cryolite	
Mn	−1.18	MnO_2 (Pyrolusite) Mn_3O_4 (Hausmannite)	Reduction of oxide with Al	$3MnO + 8Al \rightarrow 9Mn + 4Al_2O_3$

Metal	*Reduction electrode potential (V)*	*Chief ore*	*Main method of extraction*	*Equation for extraction*
Ti	−0.95	$TiO_2.FeO$ (Ilmenite) TiO_2 (Rutile)	Reduction of $TiCl_4$ with Mg or Na	$TiCl_4+2Mg \rightarrow Ti+2MgCl_2$
Zn	−0.76	ZnS (Zinc blende) $ZnCO_3$ (Calamine) ZnO (Zincite)	Reduction of ZnO with C or electrolysis of $ZnSO_4$	$ZnO+C \rightarrow Zn+CO$
Cr	−0.74	$FeO.Cr_2O_3$ (Chromite)	Reduction of Cr_2O_3 with Al	$Cr_2O_3+2Al \rightarrow 2Cr+Al_2O_3$
Fe	−0.44	Fe_2O_3 (Haematite) Fe_3O_4 (Magnetite)	Reduction of oxides with CO	$Fe_2O_3+3C \rightarrow 2Fe+3CO_2$
Co	−0.28	$CoAs_2$ (Smaltite)	Reduction of Co_3O_4 with Al	$3Co_3O_4+8Al \rightarrow 9Co+4Al_2O_3$
Ni	−0.25	NiS (Millerite)	Reduction of NiO with CO	$NiO+CO \rightarrow Ni+CO_2$
Sn	−0.14	SnO_2 (Tin stone or cassiterite)	Reduction of SnO_2 with C	$SnO_2+2C \rightarrow Sn+2CO$
Pb	−0.13	PbS (Galena)	Reduction of PbO with C	$PbO+C \rightarrow Pb+CO$
Bi	+0.32	Bi_2S_3 (Bismuth glance) Bi_2O_3 (Bismuthite)	Reduction of Bi_2O_3 with C	$Bi_2O_3+3C \rightarrow 2Bi+3CO$
Cu	+0.34	$CuFeS_2$ (Copper pyrites) Cu_2O (Cuprite)	Partial oxidation of sulphide ore	$2Cu_2O+Cu_2S \rightarrow 6Cu+SO_2$
Ag	+0.80	Native state Ag_2S (Argentite)	Leaching with cyanide	$Ag_2S+4CN^- \rightarrow 2[Ag(CN)_2]^-+S^{2-}$ $\downarrow +Zn$ $2Ag+[Zn(CN)_4]^{2-}$

Metal	*Reduction electrode potential (V)*	*Chief ore*	*Main method of extraction*	*Equation for extraction*
Hg	+0.85	HgS (Cinnabar)	Direct reduction of HgS by heating	$HgS+O_2 \rightarrow Hg+SO_2$
Pt	+1.20	Free state $PtAs_2$ (Sperrylite)	Thermal decomposition of $(NH_4)_2PtCl_6$	$(NH_4)_2PtCl_6$ $\downarrow$ $Pt+2NH_4Cl+2Cl_2$
Au	+1.50	Occurs as such	Leaching with cyanide and treating the complex with zinc	$4Au+8CN^-+2H_2O+O_2 \rightarrow$ $4[Au(CN)_2]^-+4OH^-$ $\downarrow +2Zn$ $4Au+2[Zn(CN)_4]^{2-}$

Refining of Metals

Most of the metals extracted from ores require refining because they are contaminated with undesirable impurities. The methods of refining differ from metal to metal. Some techniques that are commonly followed are outlined below:

(i) LIQUATION

This method is used for concentration as well as refining of the low melting metals. Impure metal like tin, lead or bismuth is placed at the top of a sloping hearth of a furnace. On being heated to a temperature slightly above its melting point, the metal flows down the inclined hearth while the impurities are left behind.

(ii) DISTILLATION

Low boiling metals like zinc, cadmium and mercury are purified by distillation. The pure metal distils over while the impurities are left behind in the retort.

(iii) OXIDATION

When the impurities in a metal have greater affinity for oxygen and are easily oxidized than the metal, oxidation methods are used. The various methods employed for different metals bear different names like *cupellation*, *bessimerization*, etc.

Cupellation

The impurity of lead in silver is removed by heating it in a cupel (boat-shaped shallow crucible made of bone ash or cement) under a blast of air. Lead is easily oxidized to litharge (PbO) and is carried away by the air current while pure silver is left behind.

Bessimerization

Molten pig iron from blast furnace is taken in a Bessemer converter and the impurities are oxidized by a blast of air.

(iv) POLING

The impure molten metal is stirred with green poles of wood. Hydrocarbon gases escaping from the poles act as reducing agents and reduce any oxide impurity present in the metal. For example, blister copper contains the impurity of cuprous oxide. On poling, the oxide is reduced to metallic copper.

(v) ELECTROLYTIC REFINING

This is a very widely used method for the purification of a large number of metals like copper, silver, gold, zinc, nickel, etc. The impure metal is made the anode while the thin sheet of pure metal acts as the cathode. The electrolyte is generally an aqueous solution of a salt or a complex of the metal. On passing the electric current, pure metal deposits on the cathode through the solution. The soluble impurities go into the solution while the insoluble low electropositive impurities collect as a muddy deposit (called anode mud) below the anode. The valuable metals—silver, gold and platinum—are recovered from the anode mud in the electrolytic refining of copper (Fig. 13.14).

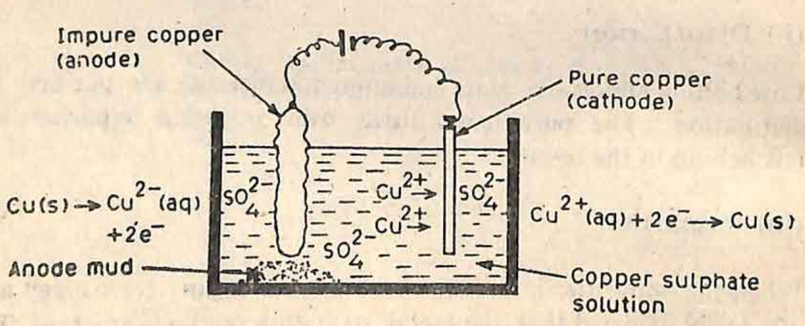


Fig. 13.14. Electrolytic refining of copper.

(vi) ZONE REFINING

When an impure metal is solidified, crystals of pure metal are deposited in preference to the impurities present which remain in the molten form. Based on this principle, *zone refining* process is used to obtain metals of very high purity.

A circular heater is fitted around a rod of an impure metal and is slowly moved along the rod (Fig. 13.15). At the heated zone, the rod melts. As the heater moves along, pure metal crystallizes out of the melt while the impurities are carried away in the molten zone to one end of the rod. The process is repeated and after several passes the impurities are completely swept to the end which is finally discarded. Semi-conductors silicon, germanium and galium are purified by this technique.

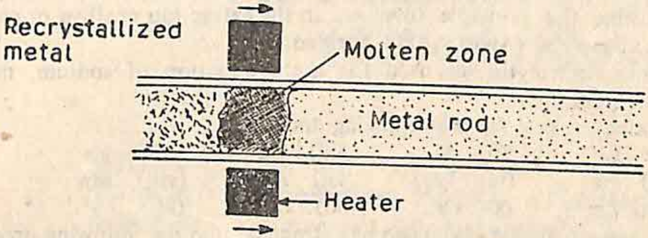


Fig. 13.15. Zone refining.

(vii) VAN ARKEL METHOD

This method is based on the thermal decomposition of a metal compound. The metal like titanium, thorium or zirconium is converted into an unstable compound, usually an iodide, and is decomposed on a hot metal filament. For example:

$$\begin{array}{ccc} \underset{\text{(Impure)}}{Zr(s)+2I_2(g)} & \longrightarrow & ZrI_4(g) \\ & & \Big\downarrow \text{Heat} \\ & & \underset{\text{(Pure)}}{Zr(s)+2I_2(g)} \end{array}$$

EXERCISES

13.1 Give the various forms in which the metals occur in nature.
13.2 Explain the following terms:

(i) Mineral (ii) Ore
(iii) Gangue (iv) Igneous rocks
(v) Sedimentary rocks (vi) Metamorphic rocks

13.3 Define metallurgy. What are the various steps involved in the metallurgy?

13.4 What do you understand by the term beneficiation of an ore? Outline the methods which are generally employed for beneficiation of an ore.

13.5 Write short notes on the following:
(i) Calcination (ii) Roasting
(iii) Smelting (iv) Aluminothermy
(v) Electrolytic reduction (vi) Leaching with cyanide solution

13.6 Outline the principle involved in the extraction of silver or gold. How can the metal (Ag or Au) be purified?

13.7 Draw electrolytic cells used for the production of sodium, magnesium and aluminium.

13.8 Name the ores for the following metals:
(i) Li (ii) K (iii) Ba (iv) Ca
(v) Na (vi) Mg (vii) Al (viii) Mn
(ix) Zn (x) Cr (xi) Fe (xii) Ni

13.9 Name the metals which can be extracted from the following ores:
(i) Cinnabar (ii) Argentite
(iii) Galena (iv) Cassiterite
(vi) Calamine (vi) Rutile
(vii) Pyrolusite (viii) Beryl

13.10 What are the various methods used in refining of the metals?

13.11 What are the methods used for purification of copper?

Unit 14

The Transition Elements (d-Block Elements)

Definition, electronic configurations and general characteristic properties: Variable oxidation states, formation of complexes, formation of coloured compounds, magnetic properties with examples from 3 d transition elements.

Metals of chromium and manganese group (general treatment only). Potassium dichromate, potassium permanganate. Metals of iron group: Iron, steel, alloy steels. Compounds of iron: Ferrous sulphate, ferrous ammonium sulphate, ferric chloride, potassium ferrocyanide. Simple treatment of corrosion. Metals of copper group: Copper and silver. Copper sulphate, silver nitrate. Alloys of Copper and silver metals and compounds of zinc group (general treatment).

Whenever we think of transition elements, certain special characteristics associated with these elements like variable oxidation state, complex formation, coloured compounds, magnetic behaviour, metallic nature and catalytic activity flash in our minds. Before discussing these features, it is appropriate to define the transition elements.

14.1. DEFINITION AND ELECTRONIC CONFIGURATIONS

The transition elements exhibit transitional behaviour between highly reactive ionic-compound forming *s*-block elements on one side and mainly covalent-compound forming *p*-block elements on the other side. It is also apparent from their position in the Periodic Table (Fig. 14. 1); the transition elements lie in between *s*- and *p*-block elements. They are also called *d*-block elements because the incoming electrons are added to the penultimate *d* level.

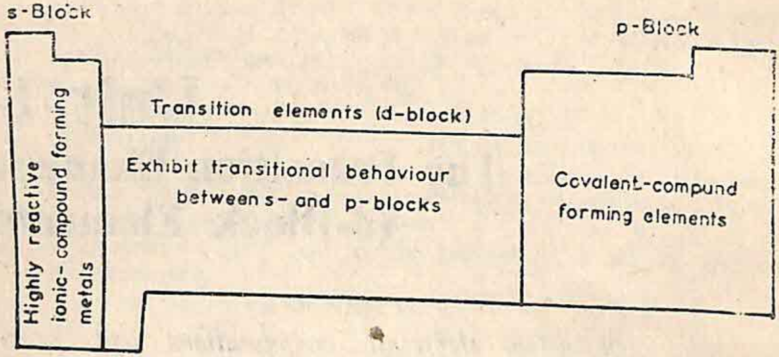

s-Block
p-Block
Highly reactive ionic-compound forming metals
Transition elements (d-block)
Exhibit transitional behaviour between s- and p-blocks
Covalent-compund forming elements

Fig. 14.1. Periodic Table showing the position of transition elements (*d*-block) in between *s*- and *p*-block elements.

There are three series of transition elements—from scandium to zinc (first series or 3 *d* series), from yttrium to cadmium (second series or 4 *d* series) and from lanthanum to mercury (third series or 5 *d* series). There is also an incomplete fourth series having actinium. The transition elements with their electronic configurations are shown in Table 14.1.

TABLE 14.1

d-Block Elements

21 Sc [Ar] $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$
39 Y [Kr] $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^1 4d^4$	42 Mo $5s^1 4d^5$	43 Tc $5s^1 4d^6$	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $5s^0 4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$
57 La [Xe] $6s^2 5d^1$	72 Hf $6s^2 5d^2$	73 Ta $6s^2 5d^3$	74 W $6s^2 5d^4$	75 Re $6s^2 5d^5$	76 Os $6s^2 5d^6$	77 Ir $6s^2 5d^7$	78 Pt $6s^1 5d^9$	79 Au $6s^1 5d^{10}$	80 Hg $6s^2 5d^{10}$
89 Ac [Rn] $7s^2 6d^1$	104	105	106	107	108	109	110	111	112

14.2. GENERAL CHARACTERISTICS

We shall now discuss the general characteristics of the transition elements.

Variable Oxidation State

The transition metals are characterized by variable oxidation states (Fig. 14.2). They have their valence electrons in two different sets of orbitals, viz., $(n-1)d$ and ns orbitals (see electronic configurations in Table 14.1). These orbitals are of comparable energies (Fig. 14.3). When ns electrons are involved, the compounds with lower oxidation states are formed. In compounds with higher oxidation states, the involvement of $(n-1)d$ electrons takes place. The highest oxidation state of an element is given by $N = ns + (n-1)d$ electrons. As the energy difference between the two sets of orbitals is not large, the transition elements exhibit variable oxidation states differing by 1 unit. The relative stabilities of these oxidation states are governed by the electronic configuration of the element, the type of bonding involved, the stereochemistry, the lattice energy, the solvation energy, the solvent, etc.

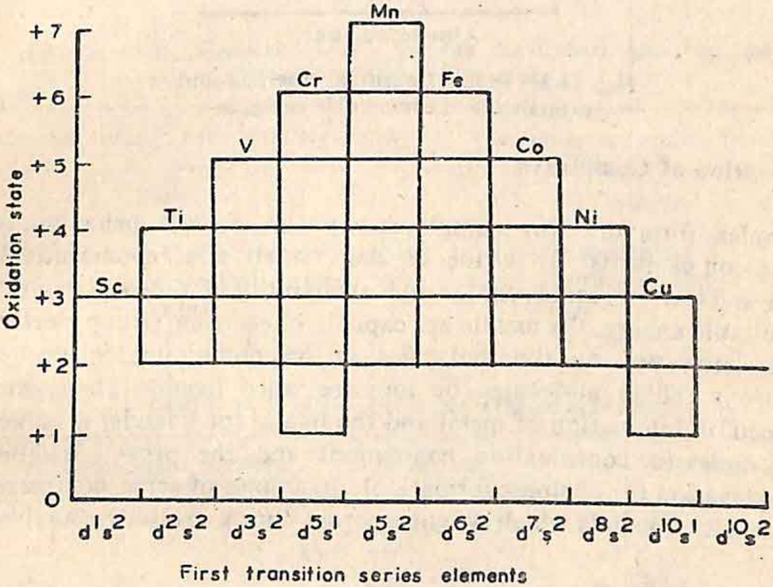


Fig. 14.2. Oxidation states of the elements of first transition series.

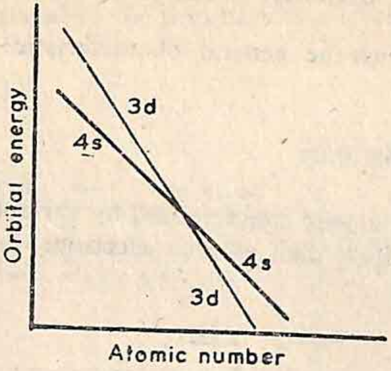


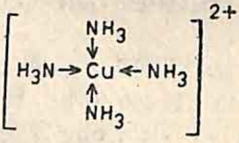
Fig. 14.3. In first transition series, *3d* and *4s* orbitals are of comparable energies.

Formation of Complexes

Complex formation (or complexation) is a typical behaviour of transition elements. By virtue of their small size, comparatively high nuclear or ionic charge and availability of vacant *d* orbitals of suitable energy, the metals are capable of exerting strong electrostatic attraction on the molecules or ions containing lone pair of electrons. These molecules or ions are called ligands. The species formed on interaction of metal and the ligand (or ligands) is known as complex (or coordination compound) and the process is called complexation (or complex formation). Examples of some complexes of transition metals which we come across during qualitative analysis are:

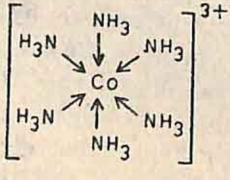
$$[H_3N \rightarrow Ag \leftarrow NH_3]^+$$

Diamminesilver(I) complex



$$\left[\begin{array}{c} NH_3 \\ \downarrow \\ H_3N \rightarrow Cu \leftarrow NH_3 \\ \uparrow \\ NH_3 \end{array}\right]^{2+}$$

Tetraamminecopper(II) complex



Hexaamminecobalt(III) complex

Formation of Coloured Compounds

Most of the transition metal ions contain unpaired *d* electrons which absorb certain wavelengths of light in the visible region and emit the remainder as coloured light. Thus the transition metal compounds are usually coloured. The relationship between the colour absorbed (in the visible region) and the complementary colour observed is given in Table 14.2. The colour of a transition metal ion may be related to the number of unpaired *d* electrons as shown in Table 14.3. It should, however, be remembered that it is not the only factor responsible for the colour.

TABLE 14.2: The Relationship between the Colour Absorbed and the Complementary Colour Observed

Colour absorbed in the visible region	*Complementary colour observed*
Violet	Yellow-green
Indigo	Yellow
Blue to blue-green	Orange to red
Green to yellow-green	Purple to violet
Orange	Blue
Red	Blue-green

TABLE 14.3: Colour of Some Transition Metal Ions

No. of unpaired electrons	*Metal ions*	*Colour observed*
0	Cu^+, Zn^{2+}, Sc^{3+}, Ti^{4+}	Colourless
1	Cu^{2+}, V^{4+}	Blue
2	Ni^{2+}, V^{3+}	Green
3	Co^{2+}	Pink
3	Cr^{3+}	Green
4	Fe^{2+}	Green
4	Cr^{2+}	Blue
5	Mn^{2+}	Pale pink
5	Fe^{2+}	Yellow

Magnetic Properties

Substances (ions, atoms or molecules) containing unpaired electrons exhibit paramagnetism, *i.e.*, they weigh more in a magnetic field. As the transition metal ions usually contain unpaired *d*-electrons, they are paramagnetic in nature. The magnetic moment increases with the number of unpaired electrons. In first transition series, magnetic moment, μ (in Bohr magneton) is related to the number of unpaired electrons, n, by the formula:

$$\mu = \sqrt{n(n+2)}$$

Based on this formula, the magnetic moments can be calculated and the values compared with those obtained experimentally (Table 14.4). It is evident that the values attain a maximum with the metal ion having largest number of unpaired electrons.

TABLE 14.4: Calculated and Observed Magnetic Moments of Some Ions of First Transition Series

Ion	*Outer electronic configuration*	*No. of unpaired electrons*	*Magnetic moment*	
			Calculated	*Observed*
Sc^{3+}, Ti^{4+}	$3d^0$	0	0	Diamagnetic
Ti^{3+}, V^{4+}	$3d^1$	1	1.73	1.7 —1.8
Ti^{2+}, V^{3+}	$3d^2$	2	2.83	2.75—2.85
V^{2+}, Cr^{3+}	$3d^3$	3	3.87	3.70—3.90
Mn^{2+}, Fe^{3+}	$3d^5$	5	5.92	5.85—5.95
Fe^{2+}, Co^{3+}	$3d^6$	4	4.90	5.1 —5.7
Co^{2+}, Ni^{3+}	$3d^7$	3	3.87	4.3 —5.2
Ni^{2+}, Cu^{3+}	$3d^8$	2	2.83	2.8 −3.5
Cu^{2+}	$3d^9$	1	1.73	1.7 −2.0
Cu^{+}, Zn^{2+}	$3d^{10}$	0	0	Diamagnetic

Other Characteristics

The general features of the first transition series are given in Table 14.5. There is a gradual decrease in atomic radii and a slow

TABLE 14.5: Some Physical Properties of the Elements of First Transition Series

Element	*Atomic radius, Å*	*Fist Ionization energy, kJ mol^{-1}*	*Electro-negativity*	*Density, g cm^{-3}*	*Melting point, K*	*Boiling point, K*
Sc	1.64	633	1.30	3.01	1812	3000
Ti	1.47	659	1.50	4.51	1951	3573
V	1.35	650	1.60	6.10	2193	3673
Cr	1.29	653	1.88	7.19	2173	2873
Mn	1.27	713	2.07	7.43	1523	2373
Fe	1.26	762	2.10	7.86	1813	2773
Co	1.25	759	2.10	8.90	1765	3173
Ni	1.25	736	2.10	8.90	1726	3093
Cu	1.28	745	2.60	8.92	1356	2853
Zn	1.37	906	2.84	7.14	692	1192

increase in first ionization energies and electronegativities. The effect of adding an electron to an inner shell in a transition element is not so pronounced as for such addition to an outer *s*- or *p*-orbital.

In transition elements, the inner orbitals become filled and the increased nuclear charge pulls the electrons in. This leads to the comparatively low atomic volumes of transition elements compared to those of the neighbouring elements of groups I and II. Consequently the densities of the transition elements are high.

It can be seen from Table 14.5 that the melting points of the elements increase nearly up to the middle of the series where they can release the largest number of valence electrons for metallic bonding. The elements in this region also exhibit the highest oxidation states.

The transition elements being quite similar in atomic sizes, they can mutually replace one another in crystal lattices. This gives rise to the formation of solid solutions and alloys. These alloys find extensive application in industry.

The tansition elements show vertical group similarities like the elements of *s*- and *p*-blocks. But in contrast to the elements of these blocks, they also show some horizontal similarities.

The transition elements are all metals and show a gradual decrease in electropositive character up to the elements of copper group. They do not displace hydrogen from acids (as one should expect from their electrode potentials) because of their surfaces being covered with inert, insoluble and sticking oxides.

The transition elements are known to form interstitial compounds by incorporating in variable ratios small non-metallic atoms in the spaces between the metal atoms. The formation of such compounds is probably the reason of catalytic activity shown by the elements. The interstitial compounds absorb and activate the reacting species. Iron, nickel, platinum and vanadium pentoxide are well known catalysts.

14.3. NOMENCLATURE OF COMPLEXES

The nomenclature system recommended by the Inorganic Nomenclature Committee of the International Union of Pure and Applied Chemistry (IUPAC) is outlined below:

(i) Non-ionic or molecular complexes are given a one word name. For example: $Co(NH_3)_3(NO_2)_3$ Trinitrotriamminecobalt (III)

(ii) The cation is named first and then the anion in accordance with the usual nomenclature rules applied to ionic salts. For example:

$NaNO_3$	Sodium nitrate (salt)
$K_2[PtCl_6]$	Potassium hexachloroplatinate(IV)

(iii) The ligands are listed in the following order: negative ligands, neutral ligands and positive ligands. Within each of these categories, the ligands are named alphabetically. For example:

$[Co(NH_3)_4(NO_2)Cl]Cl$

Chloronitrotetraamminecobalt(III) chloride

(iv) Negative ligands end in -o, neutral ligands have no special endings and positive ligands end in -ium. For example:

Negative ligands		*Neutral ligands*		*Positive ligands*	
Cl^-	Chloro	CO	Carbonyl	NO^+	Nitrosonium
OH^-	Hydroxo	H_2O	Aquo	NO_2^+	Nitronium
SO_4^{2-}	Sulphato	NH_3	Ammine	$C_5H_5N^+$	Pyridinium
$C_2O_4^{2-}$	Oxalato	NO	Nitrosyl	$NH_2\text{-}NH_3^+$	Hydrazinium

(v) The prefixes di-, tri-, tetra-, penta- and hexa- are used to indicate the number of ligands of that type. For example:

$[Cr(H_2O)_4Cl_2]NO_3$ Dichlorotetraaquochromium(III) nitrate

(vi) When the name of the ligand includes a number like di in dipyridyl or di in ethylenediamine then bis, tris and tetrakis are used to designate the number of each kind of ligand. For example:

$[Cr(en)_3]Cl_3$ Tris(ethylenediamine)chromium(III) chloride

(where en stands for ethylenediamine)

(vii) The oxidation state of the central metal is indicated by a Roman numeral in brackets immediately after its name. For example:

$[Ag(NH_3)_2]Cl$ Diamminesilver(I) chloride

(viii) When the complex is anionic, the name of the central metal ends in ate. For cationic, neutral or non-ionic complexes, the name of the central metal is used as such. For example:

$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$[Cr(H_2O)_4Cl_2]Cl$	Dichlorotetraaquochromium(III) chloride

Some more examples are given to illustrate the rules:

$[Co(NH_3)_6]Br_3$	Hexaamminecobalt(III) bromide
$[Co(NH_3)_3NO_2.Cl.CN]$	Chlorocyanonitrotriamminecobalt(III)
$K_4[Cu(CN)_6]$	Potassium hexacyanocuprate(II)
$K_3[Al(C_2O_4)_3]$	Potassium trisoxalatoaluminate(III)
$K_4[CrF_6]$	Potassium hexafluorochromate(II)

14.4. METALS OF SCANDIUM GROUP

This group consists of four elements—scandium, yitrium, lanthanum and actinium—with outer electronic configuration $(n\text{-}1)\ d^1\ ns^2$. The elements are quite reactive and form trivalent ions in their compounds. They are obtained by reduction of their chlorides. The general physical properties of the elements are given in Table 14.6.

TABLE 14.6: Some Pheysical Properties of the Elements of Scandium Group

Element	*First ionization energy, kJ mol^{1-}*	*Abundance in earth's crust, ppm*	*Melting point, K*	*Electronegativity*
Sc	633	5	1812	1.3
Y	616	28	1782	1.2
La	541	18	1193	1.1
Ac*		Trace	1325	1.1

*Radioactive element.

14.5. METALS OF TITANIUM GROUP

It comprises of three elements—titanium, zirconium and hafnium. The elements have similar electronic configuration of the type $(n\text{-}1)$ $d^2\ ns^2$, The most prominent oxidation state of the metals is +4 though they also show +2 and +3 oxidation states in their compounds. Titanium is the ninth most abundant element in the earth's crust and it is extracted from its ores rutile (TiO_2) and ilmenite ($FeTiO_3$). Some characteristics of the elements are given in Table 14.7.

TABLE 14.7; Some Physical Properties of the Elements of Titanium Group

Element	*Abundance in earth's crust, ppm*	*M.pt., K*	*Electronegativity*
Ti	4400	1951	1.5
Zr	220	2125	1.4
Hf	4.5	2495	1.3

Titanium is used as a structural material in the construction of engines, aircraft frames and marine equipment. TiO_2 and ZrO_2 are used as extra white pigments. $TiCl_4$ is used for producing smoke screens.

14.6. METALS OF VANADIUM GROUP

This group consists of vanadium, niobium and tantalum having the general electronic configuration as $(n\text{-}1)d^3ns^2$. The +5 oxidation state becomes more stable on descending the group. The metals can be obtained by electrolysis of their molten fluoro complexes. Some characteristics of the metals are given in Table 14.8.

TABLE 14.8: Some Physical Properties of the Elements of Vanadium Group

Element	*Atomic radius, Å*	*Melting point, K*	*Boiling point, K*	*Abundance in earth's crust, ppm*
V	1.35	2193	3673	150
Nb	1.47	2693	5373	24
Ta	1.47	3273	6273	2

Vanadium and its oxide (V_2O_5) are important catalysts. Vanadium and niobium are used in steel alloys. Tantalum is used for making wires, plates and screws for fractured bones.

14.7. METALS OF CHROMIUM GROUP

The elements of this group are chromium, molybdenum and tungsten. The most important oxidation states for chromium are +3 and +6 while molybdenum and tungsten usually exhibit +6 state. Some of their physical properties are summarized in Table 14.9.

Chromium is usually extracted from its ore chromite ($FeO.\ Cr_2O_3$). All the three metals are extensively used in the manufacture of steel alloys. Many of chromium compounds like sodium dichromate, potassium dichromate, ammonium dichromate, chromite and lead chromate are industrially useful. Molybdenum is used as a catalyst in the manufacture of ammonia (Haber's process). Tungsten filaments are used in incandescant lamps.

TABLE 14.9: Some Physical Properties of the Elements of Chromium Group

Element	*Atomic radius, Å*	*Melting point, K*	*Boiling point, K*	*Abundance in earth's crust, ppm*
Cr	1.29	2173	2873	200
Mo	1.40	2893	4873	15
W	1.41	3663	5973	70

14.8. CHROMIUM COMPOUNDS

The element chromium gets its name from *chroma* which means colour in Greek. Most of chromium compounds are coloured. The important compound potassium dichromate is obtained as orange-red crystals by mixing a hot saturated solution of sodium dichromate with stoichiometric amount of potassium chloride.

$$Na_2Cr_2O_7 + 2KCl \dashrightarrow K_2Cr_2O_7 + 2NaCl$$

Sodium chloride being the lest soluble precipitates out first from the hot solution and is removed by filtration. On cooling the mother liquor, crystals of potassium dichromate are obtained.

Properties

Some of its important reactions are given below:

Oxidizing Behaviour

It acts as a powerful oxidizing agent in acidic medium

$$K_2Cr_2O_7 + 4H_2SO_4 \dashrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

The reaction is used to oxidize ferrous to ferric, iodide to iodine, sulphite to sulphate and sulphide to sulphur.

$$\begin{aligned}
2Fe^{2+} + 2H^+ + (O) &\dashrightarrow 2Fe^{3+} + H_2O \\
2I^- + H_2O + (O) &\dashrightarrow 2OH^- + I_2 \\
SO_3^{2-} + (O) &\dashrightarrow SO_4^{2-} \\
S^{2-} + 2H^+ + (O) &\dashrightarrow H_2O + S
\end{aligned}$$

CHROMYL CHLORIDE TEST

Potassium dichromate reacts with chloride ions in presence of concentrated sulphuric acid to give red vapours of chromyl chloride.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 3H_2O + \underset{\text{Chromyl chloride}}{2CrO_2Cl_2}$$

This test is used to detect the presence of chlorides.

ACTION OF HEAT

On heating, potassium dichromate decomposes to green chromic oxide and oxygen.

$$4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + \underset{\text{Chromic oxide}}{2Cr_2O_3} + 3O_2$$

ACTION OF ALKALI

When heated with an alkali, dichromate forms yellow chromate.

$$Cr_2O_7^{2-}+2OH^- \longrightarrow 2CrO_4^{2-}+H_2O$$

On acidification. the reaction is reversed and we get back orange coloured dichromate.

$$2CrO_4^{2-}+2H^+ \longrightarrow Cr_2O_7^{2-}+H_2O$$

Uses

Potassium dichromate is used in dyeing, chrome tanning, calico printing and photography. It is an important volumetric reagent used for estimating ferrous salts, iodides and sulphites. Its mixture with concentrated sulphuric acid (known as chromic acid) is used in the laboratory for cleaning glass apparatus. Potassium dichromate is also used for the preparation of chromium compounds like chrome alum [$K_2SO_4,Cr_2(SO_4)_3 \cdot 24H_2O$], chrome yellow ($PbCrO_4$), chrome red ($PbCrO_4.PbO$), etc.

14.9. Metals of Manganese Group

Manganese, technetium and rhenium belong to this group. The elements are characterized with the outer electronic configuration $(n-1)d^5ns^2$. They exhibit several oxidation states in their compounds—the most important being +2 and +7 for manganese, +4 and +7 for technetium and + 3, +4 and +7 for rhenium. Some of their physical properties are given in Table 14.10.

TABLE 14.10. Some Physical Properties of the Elements of Manganese Group

Element	*Atomic radius A°*	*Melting point, K*	*Boiling point, K*	*Density, g cm⁻³*
Mn	1.27	1523	2373	7.43
Tc	1.35	2413	—	11.5
Re	1.37	3443	6173	21.0

Manganese is the tenth most abundant element (1000 ppm) in the earth's crust, It mainly occurs in the form of oxide deposits such as MnO_2 (pyrolusite), Mn_2O_3 (braunite) and Mn_3O_4 (hausmanite). The metal is obtained by reduction of the oxide with carbon or aluminium. Most of manganese produced is used in the manufacture of alloys like manganese steel, spiegeleisen, ferromanganese, manganin and manganese bronze.

14.10. Manganese Compounds

The +2 is the most stable oxidation state for manganese. The hydrated Mn^{2+} salts are pink in colour. Potassium permanganate is the most important compound of +7 manganese. It is manufactured from MnO_2. The oxide is fused with potassium hydroxide and the green melt of potassium manganate obtained is oxidized electrolytically or by passing chlorine or ozone into solution.

$$2MnO_2+4KOH+O_2 \longrightarrow \underset{\text{Potasssum manganate}}{2K_2MnO_4+2H_2O}$$

Electrolytic oxidation

$$MnO_4^{2-} \longrightarrow MnO_4^-+e^- \text{ (Anode reaction)}$$

Oxidation by chlorine or ozone

$$2MnO_4^{2-}+Cl_2 \longrightarrow 2MnO_4^-+2Cl^-$$

$$2MnO_4^{2-}+O_3+H_2O \rightarrow 2MnO_4^-+2OH^-+O_2$$

The purple solution containing potassium permanganate is concentrated by evaporation when it crystallizes out.

Properties

Purple coloured crystals of potassium permangante are fairly soluble in water. The compound is a very powerful oxidizing agent in acidic, neutral and alkaline media. The effective equations in the three media may be written as:

In acidic medium

$$MnO_4^-+8H^++5e^- \longrightarrow Mn^{2}+4H_2O$$

In neutral medium

$$MnO_4^-+2H_2O+3e^- \longrightarrow MnO_2+40H^-$$

In alkaline medium

$$MnO_4^-+e^- \longrightarrow MnO_4^{2-}$$

Manganate is further reduced to MnO_2 in presence of a reducing agent.

$$MnO_4^{2-}+2H_2O+2e^- \longrightarrow MnO_2+4OH^-$$

The complete reaction is

$$MnO_4^{2-}+2H_2O+3e^- \longrightarrow MnO_2+4OH^-$$

which is the same as in neutral medium.

In acidic medium, potassium permanganate oxidizes ferrous to ferric, oxalate to carbon dioxide, nitrite to nitrate, iodide to iodine, halogen acids to halogens, etc. Some of these reactions may be represented as:

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$
$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$
$$2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$$

When heated alone or in presence of an alkali, potassium permanganate is converted into manganate and evolves oxygen.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$
$$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

Uses

Potassium permanganate is used as an oxidizing agent in the laboratory and in industry. It is used for qualitative detection of halides, oxalates, sulphites, etc., and for volumetric estimations of Fe^{2+}, $C_2O_4^{2-}$, NO_2^-, etc. It acts as a disinfectant for water.

14.11. Metals of Group VIII

Group VIII of Periodic Table consists of three triads of transition metals. The first triad is of iron, cobalt and nickel (called *iron triad* or *iron group*), the second contains ruthenium, rhodium and palladium and the third consists of osmium, irridium and platinum. The last two triads are called *platinum triads* (Fig. 14.4).

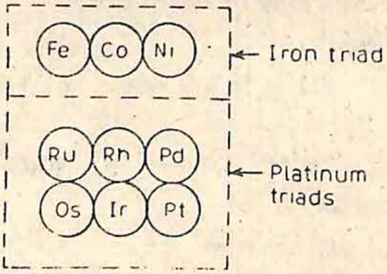


Fig. 14.4. Iron triad and platinum triads.

The elements of iron triad are comparatively reactive while those of the platinum triads are rather inert. All these metals have high melting and boiling points, exhibit variable oxidation states, form coloured complexes, show magnetic properties and act as catalysts.

Iron is the fourth most abundant element in the earth's crust (50 000 ppm) and is of immense use. We shall now discuss some aspects of this metal and its important compounds.

14.12. IRON AND STEEL

In Unit 13, we have learnt how iron is obtained from its oxide ore, haematite (Fe_2O_3). Molten iron coming out of the lower hole of the blast furnace contains about 5% carbon together with some sulphur, phosphorus, silicon and manganese. This variety of iron is called *pig iron* or *cast iron* and is the least pure form of iron. It is hard but too brittle to be used for welding or forging. It expands on solidification and, therefore, finds extensive use in casting.

There are two other varieties of iron called *steel* (carbon content between 0.2—2%) and *wrought iron* (carbon content less than 0.2%). Steel is moderately hard, less brittle, somewhat malleable and can be tempered and welded. For manufacturing steel from cast iron, the carbon content of the latter is brought down by burning away the carbon. This is done in a furnace called converter. In a recently developed method called L. D. process (Linz-Donawitz process), pure oxygen instead of air is used to oxidize impurities (Fig. 14.5). The converter is lined with magnesia to facilitate the removal of phosphorus and sulphur. Some lime is also used which acts as a flux. The oxygen, under high pressure, is introduced into the converter containing the molten cast iron. The impurities are oxidized and the temperature rises to 2300—2800K.

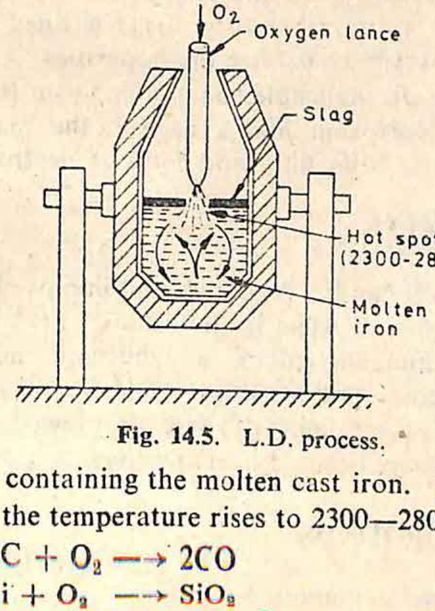


Fig. 14.5. L.D. process.

$$2C + O_2 \longrightarrow 2CO$$
$$Si + O_2 \longrightarrow SiO_2$$
$$2Mn + O_2 \longrightarrow 2MnO$$

SiO_2 reacts with MnO and CaO to form fusible $MnSiO_3$ and $CaSiO_3$ respectively.

$$MnO + SiO_2 \longrightarrow MnSiO_3$$
$$CaO + SiO_2 \longrightarrow CaSiO_3$$

The fusible slag floats on the surface of the dense iron. The purified metal is denser than the impure metal and thus the former forms the bottom layer.

The hardness of steel can be changed by heat treatment. When a steel article is heated 'to redness and then suddenly cooled by putting into water or oil, it acquires more hardness and becomes brittle. The process is called *quenching* or *hardening* of steel.

When the quenched steel is heated again between 500 and 575K and cooled slowly, its hardness remains intact but the brittleness vanishes. This process is called *tempering* or *annealing* of steel. During tempering, a very thin oxide film is formed on the surface of the steel. Depending on the thickness of the film, the surface of the steel acquires yellow or blue colour. The process helps to remove the strain present in quenched steel without affecting the hardness of the steel. The tempered steel is used for making razor blades, axes, knives, swords, etc.

Wrought iron is comparatively pure form of iron which contains less than 0.2% carbon and very small amounts of other impurities like sulphur, phosphorus, silicon and manganese. It is obtained by heating the cast iron in a reverberatory furnace lined with haematite which supplies oxygen to oxidize the impurities.

Wrought iron is soft, malleable, ductile and can be welded. It is resistant towards corrosion and is used in the manufacture of chains, anchors, wires, bolts, nails and cores of electromagnets.

14.13. ALLOY STEELS

The properties of steel can be modified and improved by addition of other metals. When the steel is alloyed with at least one metal like titanium, vanadium, chromium, molybdenum, manganese, cobalt or nickel, we obtain an *alloy steel*. The allov steels are of immense use in modern life. Some of these alloys with their composition, special characteristics and uses are given in Table 14.11.

14.14. IRON COMPOUNDS

Iron forms two series of compounds:

(i) *Ferrous* in which iron is in the divalent state, and

(ii) *Ferric* in which iron is in the trivalent state.

TABLE 14. 11. Some Important Alloy Steels

Alloy	*Percentage of component added*	*Special characteristics*	*Uses*
Stainless steel	Cr 18 Ni 8	Resists corrosion and action of organic acids	Cutlery, shaving blades, automobile parts
Nickel steel	Ni 3.5	Resists corrosion, hard and elastic	Cables, armour plates, auto and aeroplane parts
Tungsten steel	W 14-20 Cr 3-8	Very hard and corrosion resistant	High speed tools, springs
Invar	Ni 36	Very low coefficient of expansion	Tapes, watches, pendulums
Alnico	Al 12 Ni 20 Co 5	Strongly magnetic	Permanent magnets
Permalloy	Ni 78	Highly magnetised when current is passed	Electromagnets
Manganese steel	Mn 12-15	Extremely hard and tough, resistant to wear	Rock crushers, railroad tracks, safes, armour plates
Chrome vanadium steel	Cr 1 V 0.15	High tensile strength, resists corrosion and stress	Shafts, axles, springs, motor car frames

Ferrous Compounds

Ferrous sulphate, $FeSO_4.7H_2O$ (also called *green vitriol* because of its light green colour) is a very important ferrous salt. It is obtained by dissolving iron in dilute sulphuric acid and concentrating the solution to crystallization.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

On large scale, it is obtained by exposing big heaps of moist iron pyrites to air when slow oxidation converts them into ferrous sulphate.

Properties

Light green crystals of $FeSO_4.7H_2O$ are soluble in water. The aqueous solution is acidic because of the following hydrolysis taking place:

$$FeSO_4 + 2H_2O \rightleftharpoons \underset{\text{Weak base}}{Fe(OH)_2} + \underset{\text{Strong acid}}{H_2SO_4}$$

The crystals lose water and turn brown on exposure to air because of the following oxidation:

$$4FeSO_4 + 2H_2O + O_2 \longrightarrow \underset{\substack{\text{Basic ferric sulphate}\\ \text{(brown colour)}}}{4Fe(OH)SO_4}$$

Ferrous sulphate is a reducing agent and is easily oxidized by acidified potassium permanganate or dichromate. The reaction is used in volumetric estimation of ferrous ions.

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{9+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

Ferrous sulphate reacts with nitric oxide gas to form a brown compound, $FeSO_4.NO$. This forms the basis of ***brown ring test for nitrates***. When concentrated sulphuric acid is poured through the side of a test tube containing nitrate solution mixed with ferrous sulphate, a brown ring is formed at the junction of the two liquids (concentrated sulphuric acid being heavy forms the lower layer). The reaction may be represented as:

$$3Fe^{2+} + NO_3^- + 4H^+ \longrightarrow 3Fe^{3+} + NO + 2H_2O$$

$$FeSO_4 + NO \longrightarrow \underset{\text{(Brown ring)}}{FeSO_4.NO}$$

On stirring the solution, the heat of mixing of the acid increases the temperature and the brown compound is decomposed.

$$FeSO_4.NO \xrightarrow{\text{Heat}} FeSO_4 + NO$$

When a solution containing equimolar amounts of ferrous sulphate and ammonium sulphate is allowed to crystallize, it yields crystals of a double salt known as *Mohr's salt*,

$$FeSO_4.(NH_4)_2SO_4.6H_2O.$$

This salt is not easily oxidized by air and is used for preparing standard solutions of ferrous iron.

USES

Ferrous sulphate is used as a mordant in dyeing and tanning industries., It is also used in the manufacture of blue-black inks. Anhydrous ferrous sulphate is used in medicines when it supplements iron in diet.

Ferric Compounds

Ferric chloride and ferric ammonium sulphate are two important compounds of ferric iron.

Anhydrous ferric chloride is obtained by passing dry chlorine over heated iron scrap or wire (Fig. 14.6) when the salt sublimes over as deep red crystalline plates.

$$2Fe+3Cl_2 \xrightarrow{\text{Heat}} Fe_2Cl_6$$

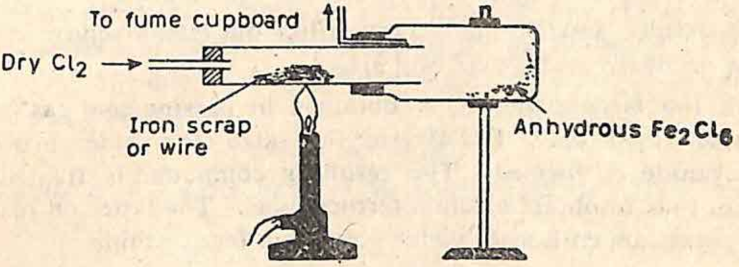
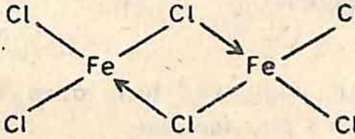


Fig. 14.6. Preparation of anhydrous ferric chloride.

PROPERTIES

In vapour state the compound corresponds to the dimer Fe_2Cl_6



Aqueous solution of ferric chloride is acidic because of the following hydrolysis :

$$FeCl_3+3H_2O \rightleftharpoons \underset{\text{Weak base}}{Fe(OH)_3} + \underset{\text{Strong acid}}{3HCl}$$

The formation of colloidal ferric hydroxide in the reaction imparts brown colour to the solution.

USES

Ferric chloride is used as a laboratory reagent and in medicines. It is also used by blockmakers for etching copper and silver.

Ferric Ammonium Sulphate

This compound which is better known as ferric alum corresponds to

$$K_2SO_4.Fe_2(SO_4)_3.24H_2O.$$

It is prepared by mixing equimolar solutions of potassium sulphate and ferric sulphate and evaporating to crystallization point. The crystals obtained are violet in colour and octahedral in shape.

Ferric alum is used as an indicator in volumetric titrations.

Potassium Ferrocyanide

In the laboratory, it can be prepared by treating ferrous sulphate with potassium cyanide.

$$FeSO_4+6KCN \longrightarrow K_4Fe(CN)_6+K_2SO_4$$

The solution is evaporated to crystallize out lemon-yellow crystals of the product, $N_4[Fe(CN)_6].3H_2O$

On the large scale, it is obtained by passing coal gas (which contains about 0.3% HCN) over hydrated iron oxide when ferric ferrocyanide is formed. The resulting compound is treated with milk of lime to obtain calcium ferrocyanide. The latter on reaction with potassium carbonate yields potassium ferrocyanide.

PROPERTIES

It reacts with cupric salts to give brown precipitate of cupric ferrocyanide.

$$2Cu^{2+} + K_4[Fe(CN)_6] \longrightarrow 4K^+ + \underset{\substack{\text{Cupric ferrocyanide}\\\text{(brown precipitate)}}}{Cu_2[Fe(CN)_6]}$$

With ferric salts, the compound form deep blue precipitate of ferric ferrocyanide called *prussian blue.*

$$4Fe^{3+} + 3K_4[Fe(CN)_6] \longrightarrow 12K^+ + \underset{\substack{\text{Ferric ferrocyanide}\\\text{(prussian blue)}}}{Fe_4[Fe(CN)_6]_3}$$

Potassium ferrocyanide can be oxidized to potassium ferricyanide by chlorine, hydrogen peroxide, ozone or potassium permanganate.

$$2K_4[Fe(CN)_6] + Cl_2 \longrightarrow 2KCl + \underset{\text{Potassium ferricyanide}}{2K_3[Fe(CN)_6]}$$

USES

Potassium ferrocyanide is used as a laboratory reagent for testing Cu^{2+}, Fe^{3+} and Zn^{2+} ions. It is also used in the manufacture of prussian blue and for making blue prints.

14.15. CORROSION

When some metals are exposed to atmospheric conditions, they may be converted into undesirable compounds (usually oxides). The process is called *corrosion*. In case of iron, corrosion is known as *rusting*.

Chemically the rust is hydrated ferric oxide, $Fe_2O_3.nH_2O$. It is non-sticking in nature and peels off exposing more of iron surface for further rusting.

Mechanism of Rusting

It is believed that the rusting takes place by an *electrochemical* process. The commercial form of iron behaves like small electric cells in presence of water containing dissolved oxygen or carbon dioxide. At the *anode* of the electrochemical cell, iron passes into solution as ferrous ions.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

At the *cathode*, the electrons from the above reaction form hydroxyl ions.

$$H_2O + (O) + 2e^- \longrightarrow 2OH^-$$

The ferrous ions and hydroxyl ions then diffuse under the influence of dissolved oxygen and ferrous ions are oxidized to ferric ions which then combine with hydroxyl ion to form hydrated ferric hydroxide, *i.e.*, rust.

$$2Fe^{2+} + H_2O + (O) \longrightarrow 2Fe^{3+} + 2OH^-$$
$$2Fe^{3+} + 6OH^- \longrightarrow Fe_2O_3.3H_2O$$

The process of rusting is represented schematically in Fig. 14.7

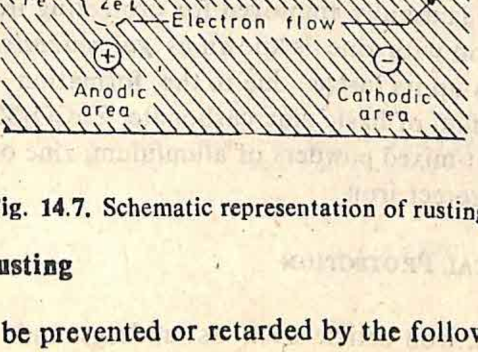


Fig. 14.7. Schematic representation of rusting.

Prevention of Rusting

The rusting can be prevented or retarded by the following methods :

It is prepared by mixing equimolar solutions of potassium sulphate and ferric sulphate and evaporating to crystallization point. The crystals obtained are violet in colour and octahedral in shape.

Ferric alum is used as an indicator in volumetric titrations.

Potassium Ferrocyanide

In the laboratory, it can be prepared by treating ferrous sulphate with potassium cyanide.

$$FeSO_4+6KCN \longrightarrow K_4Fe(CN)_6+K_2SO_4$$

The solution is evaporated to crystallize out lemon-yellow crystals of the product, $N_4[Fe(CN)_6].3H_2O$

On the large scale, it is obtained by passing coal gas (which contains about 0.3% HCN) over hydrated iron oxide when ferric ferrocyanide is formed. The resulting compound is treated with milk of lime to obtain calcium ferrocyanide. The latter on reaction with potassium carbonate yields potassium ferrocyanide.

PROPERTIES

It reacts with cupric salts to give brown precipitate of cupric ferrocyanide.

$$2Cu^{2+} + K_4[Fe(CN)_6] \longrightarrow 4K^+ + \underset{\substack{\text{Cupric ferrocyanide} \\ \text{(brown precipitate)}}}{Cu_2[Fe(CN)_6]}$$

With ferric salts, the compound form deep blue precipitate of ferric ferrocyanide called *prussian blue.*

$$4Fe^{3+} + 3K_4[Fe(CN)_6] \longrightarrow 12K^+ + \underset{\substack{\text{Ferric ferrocyanide} \\ \text{(prussian blue)}}}{Fe_4[Fe(CN)_6]_3}$$

Potassium ferrocyanide can be oxidized to potassium ferricyanide by chlorine, hydrogen peroxide, ozone or potassium permanganate.

$$2K_4[Fe(CN)_6] + Cl_2 \longrightarrow 2KCl + \underset{\text{Potassium ferricyanide}}{2K_3[Fe(CN)_6]}$$

USES

Potassium ferrocyanide is used as a laboratory reagent for testing Cu^{2+}, Fe^{3+} and Zn^{2+} ions. It is also used in the manufacture of prussian blue and for making blue prints.

14.15. CORROSION

When some metals are exposed to atmospheric conditions, they may be converted into undesirable compounds (usually oxides). The process is called *corrosion*. In case of iron, corrosion is known as *rusting*.

Chemically the rust is hydrated ferric oxide, $Fe_2O_3.nH_2O$. It is non-sticking in nature and peels off exposing more of iron surface for further rusting.

Mechanism of Rusting

It is believed that the rusting takes place by an *electrochemical* process. The commercial form of iron behaves like small electric cells in presence of water containing dissolved oxygen or carbon dioxide. At the *anode* of the electrochemical cell, iron passes into solution as ferrous ions.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

At the *cathode*, the electrons from the above reaction form hydroxyl ions.

$$H_2O + (O) + 2e^- \longrightarrow 2OH^-$$

The ferrous ions and hydroxyl ions then diffuse under the influence of dissolved oxygen and ferrous ions are oxidized to ferric ions which then combine with hydroxyl ion to form hydrated ferric hydroxide, *i.e.*, rust.

$$2Fe^{2+} + H_2O + (O) \longrightarrow 2Fe^{3+} + 2OH^-$$

$$2Fe^{3+} + 6OH^- \longrightarrow Fe_2O_3.3H_2O$$

The process of rusting is represented schematically in Fig. 14.7

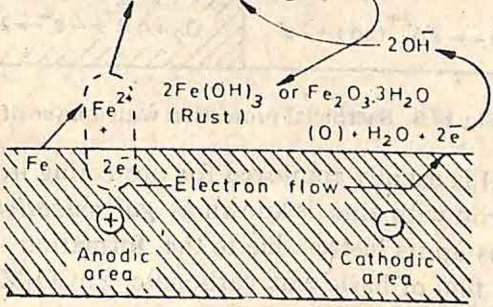


Fig. 14.7. Schematic representation of rusting.

Prevention of Rusting

The rusting can be prevented or retarded by the following methods :

(*i*) BARRIER PROTECTION

A barrier film is introduced between iron and atmospheric air. The film prevents iron from rusting. Barrier protection may be achieved by painting, varnishing or electroplating with a metal like tin, copper, chromium or nickel. Electroplated iron is prevented from rusting and it also acquires brightness. Ships, cars, bridges and other construction work all are protected by painting. The scratches or cracks in the barrier film initiate the rusting which spreads below the film.

(ii) SACRIFICIAL PROTECTION

Iron is protected by covering it with a layer of more active metal like zinc. This active metal loses electrons in preference to iron and is consumed in due to course of time. So long it remains on the surface of iron, it prevents the latter from rusting. This process of preventing the rust formation is called ***sacrificial protection.*** It is shown schematically in Fig 14.8.

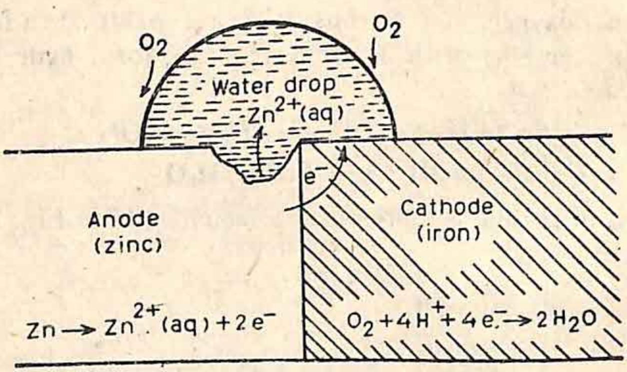

O_2
O_2
Water drop
$Zn^{2+}(aq)$
e^-
Anode
(zinc)
Cathode
(iron)
$Zn \rightarrow Zn^{2+}(aq) + 2e^-$
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Fig 14.8. Sacrificial protection with a layer of zinc

Zinc metal is usually employed for protecting iron. The process of covering iron with zinc is known as ***galvanization.*** The galvanized iron keeps up its lustre due to the formation of a protective invisible thin film of basic zinc carbonate, $ZnCO_3.Zn(OH)_2$, on the zinc film. Paint-mixed powders of aluminium, zinc or magnesium are also used to protect iron.

(*iii*) ELECTRICAL PROTECTION

In this method, iron article such as underground pipes, etc., are connected with a more active metal like magnesium, zinc or aluminium. The more active metal acts as anode and loses electrons in preference to iron and thereby protects the latter from being rusted (Fig. 14.9).

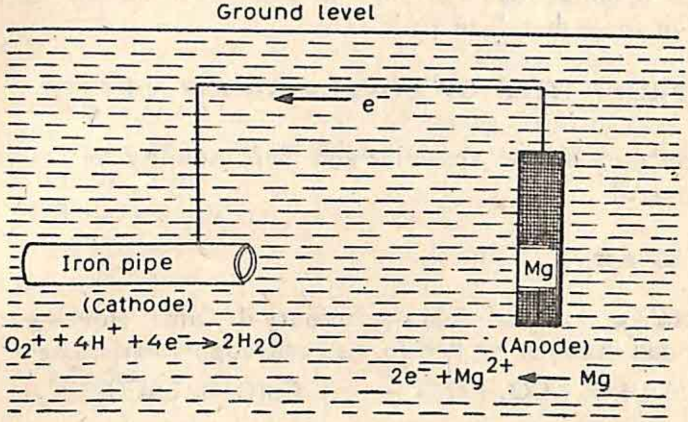

Ground level
e^-
Iron pipe
(Cathode)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
Mg
(Anode)
$2e^- + Mg^{2+} \leftarrow Mg$

Fig. 14.9. Electrical protection of iron pipes by using magnesium metal.

(iv) USE OF ANTI-RUST SOLUTIONS

Alkaline phosphate and alkaline chromate solutions are used as anti-rust solutions. For example, when iron articles are dipped into a boiling and strongly alkaline sodium phosphate solution, a protective insoluble sticking film of basic iron phosphate is formed. The film protects the articles from rusting.

14.16. METALS OF COPPER GROUP

Copper, silver and gold belong to this group. Their general electronic configuration is $(n-1)d^{10}ns^1$. They have one *s* electron in their outer orbital but differ from elements of group IA in that the penultimate shell contains 10 *d* electrons. The metals possess the highest thermal and electrical conductivities. Some of their physical properties are given in Table 14.12.

TABLE 14.12: Some Physical Properties of the Elements of Copper Group

Element	*Atomic radius,* Å	*Melting point, K*	*Boiling point, K*	*Abundance in earth's crust, ppm*
Cu	1.28	1356	2853	70
Ag	1.44	1234	2453	0.1
Au	1.44	1336	2933	0.005

Copper is mainly extracted from its sulphide ore. The important ores of silver are horn silver, AgCl and silver glance, Ag_2S. It also occurs in the native form. Gold is mostly mined in native state. In combined form it occurs as gold telluride, $AuTe_3$. It is also recovered from anode mud. We have already studied the metallurgies of these metals in Unit 13.

14.17. PROPERTIES OF COPPER GROUP METALS

The metals are not very reactive and their nobility increases from $Cu \rightarrow Ag \rightarrow Au$.

Action of Air

The metals are not attacked by ordinary dry air However, copper is corroded in moist air and forms basic copper carbonate.

$$Cu+O_2+CO_2+H_2O \longrightarrow Cu(OH)_2.CuCO_3$$

When heated in air, copper forms cupric oxide below 1400K and cuprous oxide above 1400K.

$$2Cu+O_2 \xrightarrow{\text{Below 1400K}} 2CuO$$

$$4Cu+O_2 \xrightarrow{\text{Above 1400K}} 2Cu_2O$$

Action of Water

Only at white heat temperature, copper decomposes steam.

$$2Cu + H_2O \longrightarrow Cu_2O + H_2$$

Action of Acids

Dilute sulphuric acid and hydrochloric acid do not attack copper unless air is present. In presence of air, the reactions are:

$$2Cu+\underset{\text{(Dilute)}}{2H_2SO_4}+O_2 \longrightarrow 2CuSO_4+2H_2O$$

$$2Cu + \underset{\text{(Dilute)}}{4HCl} + O_2 \longrightarrow 2CuCl_2+2H_2O$$

Silver and gold do not react even in presence of air.

Dilute nitric acid reacts with copper and silver.

$$3Cu+\underset{\text{(Dilute)}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2+2NO+4H_2O$$

$$3Ag+\underset{\text{(Dilute)}}{4HNO_3} \longrightarrow 3AgNO_3+NO+2H_2O$$

Hot concentrated sulphuric acid reacts with copper and silver but not with gold.

$$\underset{\text{(Conc.)}}{Cu+2H_2SO_4} \longrightarrow CuSO_4+SO_2+2H_2O$$

Reactions of copper and silver with concentrated nitric acid are:

$$\underset{\text{(Conc.)}}{Cu+4HNO_3} \longrightarrow Cu(NO_3)_2+2NO_2+2H_2O$$

$$\underset{\text{(Conc.)}}{Ag+2HNO_3} \longrightarrow AgNO_3+NO_2+H_2O$$

Gold reacts only with aqua regia (3 parts concentrated hydrochloric acid and 1 part concentrated nitric acid) where nitric acid acts as oxidizing agent.

$$3HCl+HNO_3 \equiv NOCl+2H_2O+2Cl$$

$$Au+3Cl+HCl \longrightarrow HAuCl_4$$

The net reaction is:

$$2Au+11HCl+3HNO_3 \longrightarrow 2HAuCl_4+6H_2O+3NOCl$$

Action of Alkalis

Copper group metals do not react with alkalis.

Action of Hydrogen Sulphide

Hydrogen sulphide present in atmosphere or as such can react with copper to form copper sulphide, CuS, and with silver to form silver sulphide, Ag_2S.

Action of Ammonia

Copper reacts with ammonia solution in presence of air to form deep blue tetraamminecopper(II) hydroxide.

$$2Cu+8NH_3+2H_2O+O_2 \longrightarrow \underset{\text{Tetraamminecopper(II) hydroxide}}{2[Cu(NH_3)_4](OH)_2}$$

Action of Cyanides

The metals react with cyanide solution in presence of air and form soluble complexes.

$$2Cu+10CN^-+O_2+2H_2O \longrightarrow 2[Cu(CN)_4]^{3-}+4OH^-+C_2N_2$$

$$4M+8CN^-+O_2+2H_2O \longrightarrow 4[M(CN)_2]^-+4OH^-$$

(where M=Ag or Au)

Action of Ozone

Copper and silver react with ozone but gold does not.

$$Cu+O_3 \longrightarrow CuO+O_2$$

$$2Ag+O_3 \longrightarrow Ag_2O+O_2$$

$$Ag_2O+O_3 \longrightarrow \underset{\text{(Black)}}{2Ag+2O_2}$$

Displacement Reactions

From the positions of copper, siver and gold in electrochemical series, it is evident that copper can displace silver and gold from their salt solutions, silver can displace gold from its salt solution but gold remains the least reactive.

14.18. USES OF COPPER GROUP METALS

Because of good conductance, copper is used for conveying electrical power and for manufacturing electrical goods. As such or in form of alloys, the metal has wide variety of uses (Table 14.13). Many of copper salts are also very useful.

Silver as such or alloyed silver (Table 14.13) is used in jewellery. Silver salts are used in silvering of mirrors, photography and in medicines. Silver leaves are used in Ayurvedic and Unani systems of medicines as a tonic.

TABLE 14.13. **Some Important Alloys of Copper, Silver and Gold**

Alloy	*Component percentage*	*Special characteristics*	*Uses*
Brass	Cu 60-80 Zn 20-40	Hard, malleable, ductile, tenacious	Utensils, casting, tubes, catridges
Bronze	Cu 75-90 Sn 10-25	Hard, tenacious, durable resists corrosion	Statues, valves, machine parts
Aluminium bronze	Cu 90 Al 10	Light, strong, resists corrosion, tenacious	Utensils, cheap jewellery, golden powder for paints
Phosphor bronze	Cu 95 Sn 4.8 P 0.2	Hard, tough, resists corrosion, elastic	Springs, suspension wires, aerials, gears, propellors
Silca bronze	Cu 97 Sn 2 Si 1	Hard, tenacious, good conductor, resists corrosion	Telephone and telegraph wires
Gun metal	Cu 88 Sn 10 Zn 2	Hard, strong, resists corrosion	Guns, cannons, gears, bearings
German silver	Cu 25-50 Zn 25-35 Ni 10-35	White shining, malleable, ductile, resists corrosion	Utensils, jewellery, resistance wire
Silver copper alloy	Ag 92.5 Cu 7.5	Hard, white shining, malleable	Silverwares, coins, jewellery
Gold copper alloy	Au 90 Cu 10	Hard, malleable, durable resists corrosion	Jewellery, spectacle rims, coins

Gold as such or its alloy with copper (Table 14.13) is used in jewellery. Gold is an article of wealth. Gold has been used in coins and in covering temple domes. Purity of gold is generally given on the *carat* scale – pure gold is 24 carat.

14.19. COMPOUNDS OF COPPER

Copper forms compounds in which its oxidation state is +1 (called *cuprous* compounds) or +2 (called *cupric* compounds).

Cuprous Compounds

Cuprous compounds are not stable in aqueous solution in which they disproportionate to copper and cupric ions.

$$2Cu^{+}(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$$

They can be stabilized by formation of insoluble compounds like cuprous halides, cuprous thiocyanate, etc., or by complex formation with halides, cyanides and ammonia.

$$CuCl + Cl^{-} \longrightarrow [CuCl_2]^{-}$$

$$CuCN + CN^{-} \longrightarrow [Cu(CN)_2]^{-}$$

$$CuCl + 2NH_3 \longrightarrow [Cu(NH_3)_2]Cl$$

When a cupric salt solution is treated with potassium iodide, cuprous iodide is precipitated.

$$2Cu^{2+} + 4I^{-} \longrightarrow 2CuI + I_2$$

The liberated iodine in the reaction is titrated against thiosulphate to estimate the strength of copper solution.

The formation of insoluble cuprous thiocyanate, CuCNS, is used in the gravimetric determination of copper.

Cupric Compounds

Copper sulphate, $CuSO_4.5H_2O$, commonly known as *blue vitriol* is an important compound of copper in which its oxidation state is +2. It is obtained by treating scrap copper with hot dilute sulphuric acid in presence of air.

$$2Cu + 2H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + 2H_2O$$

Blue crystalline copper sulphate is soluble in water. Its aqueous solution is acidic in nature due to the following hydrolysis:

$$CuSO_4 + 2H_2O \longrightarrow \underset{\text{Weak base}}{Cu(OH)_2} + \underset{\textbf{Strong acid}}{H_2SO_4}$$

On exposure to dry air, the blue crystals effloresce to a pale blue powder, $CuSO_4.3H_2O$ which changes to bluish white $CuSO_4.H_2O$ on being heated to 375K. The monohydrate becomes white anydrous $CuSO_4$ at 525K.

$$\underset{\text{(Blue)}}{CuSO_4.5H_2O} \overset{\text{Exposure}}{\rightleftharpoons} \underset{\text{(Pale blue)}}{CuSO_4.3H_2O} \overset{\text{375K}}{\rightleftharpoons} \underset{\text{(Bluish white)}}{CuSO_4.H_2O} \overset{\text{525K}}{\rightleftharpoons} \underset{\text{(White)}}{CuSO_4}$$

At above 1000 K copper sulphate decomposes to cupric oxide and sulphur trioxide.

$$CuSO_4 \longrightarrow CuO+SO_3$$

Blue colour of aqueous cupric solution is due to the presence of $[Cu(H_2O)_4]^{2+}$ ions. In ammonia solution, cupric ions form tetraamminecopper(II) ions which are deep blue in colour.

Copper sulphate is extensively used in electroplating, batteries and as a mordant for dyeing. A mixture of copper sulphate and lime under the name *Bordeaux mixture* is used as a fungicide in agriculture.

Another cupric compound known as *verdigris* (basic copper acetate) is prepared by exposing copper plates to the action of vinegar and air.

$$2Cu+2CH_3COOH+O_2 \longrightarrow \underset{\text{Verdigris}}{Cu(CH_3COO)_2.Cu(OH)_2}$$

This compound is used in the manufacture of green paints, dyeing and calico printing.

14.20. COMPOUNDS OF SILVER

Silver nitrate and silver halides are important compounds of silver.

Silver Nitrate

It is prepared by dissolving silver metal in warm dilute nitric acid.

$$3Ag+4HNO_3 \longrightarrow 3AgNO_3+2H_2O+NO$$

Colourless crystals of silver nitrate are highly soluble in water. The compound decomposes on heating as shown below:

$$2AgNO_3 \xrightarrow{\text{About 500K}} 2AgNO_2+O_2$$

$$2AgNO_3 \xrightarrow{\text{Above 1000 K}} 2Ag+2NO_2+O_2$$

Silver nitrate is an important laboratory **reagent and is used for** detection of many anions like halides, **thiosulphate, sulphide, chromate** and phosphate.

$Ag^+ + Cl^- \longrightarrow AgCl$

(White precipitate soluble in ammonium hydroxide)

$Ag^+ + Br^- \longrightarrow AgBr$

(Pale yellow ppt. slightly soluble in NH_4OH)

$Ag^+ + I^- \longrightarrow AgI$

(Yellow ppt. insoluble in ammonium hydroxide)

$2Ag^+ + S_2O_3^{2-} \longrightarrow Ag_2S_2O_3$

(White ppt. turning yellow, brown and black)

$2Ag^+ + S^{2-} \longrightarrow Ag_2S$

(Black precipitate)

$2Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$

(Brick red precipitate)

$3Ag^+ + PO_4^{3-} \longrightarrow Ag_3PO_4$

(Yellow precipitate soluble in ammonium hydroxide)

It is also used for volumetric and gravimetric determinations of halide ions. In industry, the salt finds many applications. It is used in silvering of mirrors and silver plating, preparing inks for clothes, hair dyes and medicines.

Silver Halides

All the four silver halides, *i.e.*, AgF, AgCl, AgBr and AgI, are known. Except the fluoride, others are quite insoluble. Silver bromide is soluble in concentrated thiosulphate solution due to complex formation:

$$AgBr + 2S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Br^-$$

This reaction is used in fixing the image on the photographic film since the thiosulphate dissolves away the unaffected silver bromide from the exposed film. Silver halides (except silver iodide) are light sensitive and these are used in making photographic films.

14.21. METALS OF ZINC GROUP

Metals of this group are zinc, cadmium and mercury. Their characteristic electronic configuration is $(n-1)\ d^{10}\ ns^2$, The *d* shell being complete, the metals show few properties which are associated with the transition metals. The reactivity decreases as we move from zinc to cadmium to mercury. Some physical properties of the metals are given in Table 14.14.

TABLE 14.14: Some Physical Properties of the Elements of Zinc Group

Element	*Atomic radius,* Å	*Melting point, K*	*Boiling point, K*	*Abundance in earth's crust, ppm*
Zn	1.37	692	1192	132
Cd	1.52	594	1051	0.15
Hg	1.52	234	630	0.5

In presence of moist air, zinc and cadmium get coated with a protective layer of oxide which changes to basic carbonate in due course of time. The metals burn in air to form oxides of the type MO (where M=Zn, Cd or Hg). They also combine with sulphur and halogens. Zinc and cadmium react with dilute acids to liberate hydrogen. Mercury reacts with oxidizing acids:

$$6Hg + \underset{\text{(Dilute)}}{8HNO_3} \longrightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

$$Hg + \underset{\text{(Conc.)}}{4HNO_3} \longrightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

Only zinc reacts with alkalies liberating hydrogen and forming soluble zincates.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$$

Zinc is used to galvanize iron for protecting the latter from rusting. Many zinc alloys (Table 14.13) find a variety of applications. Zinc is used as the cathode in dry cell batteries. Its oxide, obtained by burning the metal, is used as a pigment in paints and for reinforcing rubber.

Cadmium is used for electroplating steel and in the manufacture of storage batteries and some low melting alloys.

Mercury is extensively used in thermometers, barometers, electrical switches and arc lights. Organomercury compounds are used as fungicides and as timber preservatives. Sodium and zinc amalgams (alloys of mercury with sodium and zinc) are used as reducing agents.

14.22. COMPOUNDS OF ZINC GROUP METALS

We shall now consider some important compounds of zinc group metals.

Lithopone

The white pigment *lithopone*, which consists of ZnS and $BaSO_4$, is obtained by treating zinc sulphate solution with barium sulphide.

$$BaS + ZnSO_4 \longrightarrow BaSO_4 + ZnS$$

It has a good covering power and is used in the manufacture of white paints.

Cadmium Sulphide

The yellow pigment cadmium sulphide is obtained by passing hydrogen sulphide gas through a cadmium salt solution.

$$Cd^{2+} + H_2S \longrightarrow CdS + 2H^+$$

It is used as a yellow pigment in making oil and water colours.

Corrosive Sublimate

It is mercuric chloride and is obtained by heating mercury in chlorine.

$$Hg + Cl_2 \longrightarrow HgCl_2$$

It is corrosive in action and can easily sublime. It is thus known as *corrosive sublimate.*

The compound is used as an antiseptic and as a preservative for wood and skin.

Mercury Sulphide

It is of two varieties—black and red. The compound can be obtained by rubbing mercury and sulphur together.

$$Hg + S \longrightarrow HgS$$

The red variety is used as a pigment and as a cosmetic under the name *vermilion.* It is also used in Ayurvedic medicines.

Nessler's Reagent

When potassium iodide is added to mercuric chloride solution, a yellow precipitate of mercuric iodide is obtained. This dissolves in excess of potassium iodide to give potassium tetraiodomercurate(II).

$$HgCl_2 + 2KI \longrightarrow 2KCl + HgI_2$$

$$HgI_2 + 2KI \longrightarrow \underset{\text{Potassium tetraiodomercurate(II)}}{K_2[HgI_4]}$$

Alkaline solution of $K_2[HgI_4]$ is called *Nessler's reagent.* This reagent is used for testing ammonia or ammonium salts. The test is very sensitive and is shown by the appearance of brown colour or precipitate when the two react together.

EXERCISES

14.1 What are transition metals? Mention their important characteristics.

14.2 How do the electronic configurations of transition metals differ from those of *s*- and *p*-block elements?

14.3 Why do transition elements exhibit variable oxidation states? What is the highest oxidation state achieved by a transition element?

14.4 What is a complex? Why do transition elements form complexes?

14.5 Why are the transition metal compounds coloured? Is there any relation between colour of a transition metal ion and the number of unpaired d electrons present?

14.6 What is paramagnetism? What is the relation between magnetic moment and the number of unpaired electrons of a 3*d* element?

14.7 Discuss the following properties of transition elements:
(i) Density.
(ii) Melting and boiling points.
(iii) Catalytic activity.

14.8 Name the following compounds according to IUPAC rules:
(i) $Na_3[Co(NO_2)_6]$
(ii) $Na[Ag(S_2O_3)_2]$
(iii) $K_3[Mo(CN)_8]$
(iv) $[Co(NH_3)_4(NO_2)Cl]Cl$
(v) $K_4[Fe(CN)_6]$

14.9 What are the metals of chromium group? Give their general characteristics.

14.10 How will you prepare potassium dichromate? What are its uses?

14.11 Name the elements of manganese group and briefly describe their characteristics.

14.12 How will you prepare potassium permanganate? Give equations of its oxidizing behaviour in acidic, alkaline and neutral media.

14.13 Name the elements which belong to Group VIII of the Periodic Table. Which is the most abundant element among them?

14.14 What are the three varieties of iron? Which one is the most pure form of the metal?

14.15 Give preparation, properties and uses of the following compounds:
(i) Mohr's salt.
(ii) Ferric chloride.
(iii) Potassium ferrocyanide.

14.16 How will you represent rust chemically? Explain the mechanism of rusting.

14.17 Briefly describe the methods of preventing rust formation.

14.18 What are copper group metals? Give their general characteristics.

14.19 What is blue vitriol? Give its method of preparation, important properties and uses.

14.20 How is silver nitrate prepared? What are its analytical applications?

14.21 What are the metals of zinc group? Do they show properties of transition metals? Give their important characteristics.

14.22 Write short notes on the following:
(i) Quenching
(ii) Annealing
(iii) Nessler's reagent
(iv) Corrosive sublimate
(v) Alloys

Unit 15

Alkyl and Aryl Halides

Nomenclature. Isomerism, optical isomerism. General methods of preparation and properties of alkyl and aryl halides. Preparation of chloroform and iodoform,

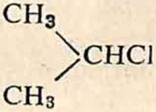
Alkyl halides are the compounds in which a halogen is bonded to an aliphatic carbon. These may be represented by the general formula RX (where R= alkyl group and X = halogen atom). The compounds are obtained by the replacement of one hydrogen atom of an alkane by a halogen atom.

$$\underset{\text{Alkane}}{RH} + X_2 \dashrightarrow \underset{\text{Alkyl halide}}{RX} + HX$$

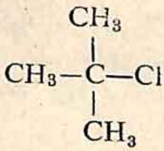
Alkyl halides may be classified as primary, secondary or tertiary halides to a primary, secondary if the halogen is attached or tertiary carbon atom. For example:

$CH_3-CH_2-CH_2Cl$

n-Propyl chloride



iso-Propyl chloride

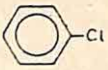


$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-Cl$$

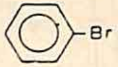
tert-Butyl chloride

Alkyl fluorides are quite different from other alkyl halides in the methods of preparation and properties. Therefore, they are dealt in separately. Here, in this Unit, we shall confine ourselves with alkyl chlorides, bromides and iodides.

Aryl halides are the compounds in which a halogen atom is linked directly to an aromatic ring by the replacement of a hydrogen atom. For example:

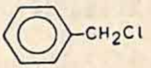


Chlorobenzene

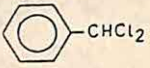


Bromobenzene

The compounds in which the halogen is in the side chain are regarded as aryl substituted *alkyl* halides and not as *aryl* halides. For example:



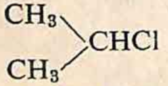
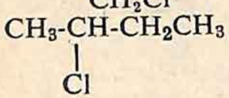
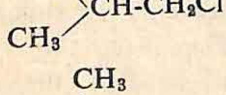
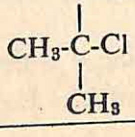
Benzyl chloride



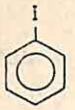
Benzal chloride

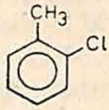
15.1. NOMENCLATURE

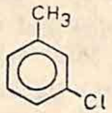
There are two systems of naming alkyl halides. In the *common* or *trivial system* they are named as halides of the corresponding alkyl groups. In the *IUPAC system*, alkyl halides are named as substitution products of the corresponding alkanes. The name of the halogen precedes that of the alkane and position is indicated by the lowest possible number. The common and IUPAC names of some alkyl halides are given below:

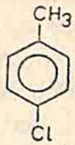
Formula	*Common name*	*IUPAC name*
CH_3Cl	Methyl chloride	Chloromethane
CH_3CH_2Br	Ethyl bromide	Bromoethane
$CH_3CH_2CH_2I$	*n*-Propyl iodide	1-Iodopropane
 $\begin{matrix}CH_3\diagdown \\ \quad CHCl \\ CH_3\diagup\end{matrix}$	*iso*-Propyl chloride	2-Chloropropane
$CH_3CH_2CH_2$ CH_2Cl	*n*-Butyl chloride	1-Chlorobutane
 $\begin{matrix}CH_3\text{-}CH\text{-}CH_2CH_3 \\ \vert \\ Cl\end{matrix}$	*sec*-Butyl chloride	2-Chlorobutane
 $\begin{matrix}CH_3\diagdown \\ \quad CH\text{-}CH_2Cl \\ CH_3\diagup\end{matrix}$	*iso*-Butyl chloride	1-Chloro-2-methyl-propane
 $\begin{matrix}CH_3 \\ \vert \\ CH_3\text{-}C\text{-}Cl \\ \vert \\ CH_3\end{matrix}$	*tert*-Butyl chloride	2-Chloro-2-methyl-propane

Aryl halides are named by prefixing the halogen and its position, if necessary, to the name of the parent aromatic compound. For example:


Iodobenzene


o-Chlorotoluene


m-Chlorotoluene


p-Chlorotoluene

15.2. ISOMERISM

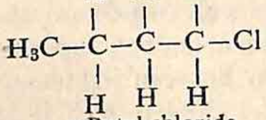
We are already familiar with the concept of isomerism. The compounds which have the same molecular formula but differ from one another in properties are called isomers and phenomenon is known as isomerism. There are two main types of isomerism—*Structural isomerism* and *stereoisomerism*.

Structural Isomerism

It is due to the different arrangement of atoms within the molecules. Here, the spatial arrangement of atoms is not taken into consideration. Alkyl halides show two types of structural isomerism: *chain isomerism* and *position isomerism*.

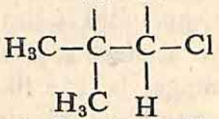
Chain Isomerism

In this type of isomerism, the isomers differ from each other in the structure of the carbon chain forming the skeleton of the molecule. For example:



$$H_3C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-Cl$$

n-Butyl chloride



$$H_3C-\overset{H}{\underset{H_3C}{C}}-\overset{H}{\underset{H}{C}}-Cl$$

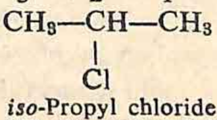
iso-Butyl chloride

Position Isomerism

In this type of isomerism, the isomers differ from each other in the position occupied by functional atom or group present in their molecules; the carbon skeleton remains the same. For example:

$$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-Cl$$

n-Propyl chloride
(Cl attached to C-1)



$$\overset{3}{CH_3}-\underset{Cl}{\overset{2}{CH}}-\overset{1}{CH_3}$$

iso-Propyl chloride
(Cl attached to C-2)

Stereoisomerism

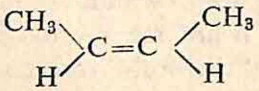
This isomerism arises because of the difference in the arrangements of atoms or groups in the space. It is of two types; *Geometrical isomerism (cis-trans isomerism)* and *optical isomerism.*

Geometrical isomerism. This type of isomerism is met in certain compounds which contain a carbon-carbon double bond and each carbon is attached to two different atoms or groups. In general, all unsaturated compounds having the formula,

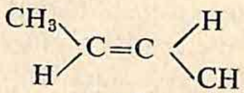
$$C_{ab}=C_{xy} \qquad \text{or} \qquad C_{ab}=C_{ab}$$

show such an isomerism.

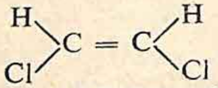
When the two carbon atoms are joined by a double bond, there is restricted free rotation between them. In this way, the atoms or groups become fixed up in two ways in space. When similar groups are attached to the same side of molecule, it is called a *cis*-isomer, while in *trans*-isomer, similar groups lie on the opposite sides. Geometrical isomerism is also known as *cis-trans isomerism.* For example:



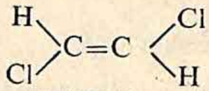
cis-2-Butene



trans-2-Butene



cis-1,2-Dichloroethene



trans-1,2-Dichloroethene

Optical Isomerism

This type of isomerism is shown by molecules which are *dissymetric.* A dissymetric molecule is that which cannot be superimposed on its mirror image. It is a like relation between right hand and left hand. Right hand is a mirror image of the left but the two hands cannot be placed one over the other in a coinciding manner. Now, let us try to understand this phenomenon of optical isomerism.

Ordinary light consists of wave motion and the vibrations are taking place in all planes at right angles to the direction of its transmission (Fig. 15.1). If the light is passed through a Nicol prism, made of a particular crystalline form of $CaCO_3$ (known as calcite), the wave motion is restricted to one plane only and the light is said to be *plane polarised* (Fig. 15.2) and the plane along which the vibrations take place is called the *plane of polarisation.* The Nicol prism used is called the *polariser.* If another Nicol prism is placed such that its axis is parallel to the polariser, the path of polarised light is not changed and it reaches the eye. This second Nicol prism is called the *analyser*. If the axis of the analyser is fixed at right angle to that of the polariser, the light is completely cut off

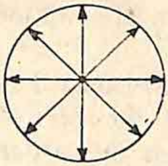


Fig. 15.1. Ordinary light consisting of vibrations in all planes at rightangles to the direction of its transmission.

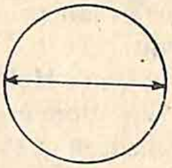


Fig. 15.2. Plane polarised light consisting of vibrations in one plane only.

and the field of view becomes dark. Let us fix polariser and analyser at right angle axis and place a glass tube filled with a solution of an organic compound in between them. The light will now reach the eye though in a very feeble intensity. It shows that the substance in solution has rotated the plane of the polarised light through a certain angle. Such substances which in solution rotate the plane of polarised light are called *optically active* and the characteristic is known as *optical activity*.

It is established that a substance which shows optical activity generally exists in two forms. These isomeric forms resemble one another in their chemical reactions and most of their physical properties but differ in their effect on polarised light. The form which rotates the plane of polarised light to the right is called *dextro rotatory* or (+) form and the other rotates to the left is called *laevo rotatory* or (−) form. Such isomers are called *optical isomers* and the phenomenon is known as *optical isomerism.*

ENANTIOMERISM

It is the simplest kind of optical isomerism. It was discovered by Pasteur in 1849. He observed that sodium ammonium tartrate existed as a mixture of two different kinds of crystals which were mirror images to each other. He separated the mixture into two parts—one of right-handed crystals and the other of left-handed crystals. Both forms were found to have the same physical and chemical properties and also optically active. They rotated the plane of polarised light equally but in opposite direction. These isomers are called *enantiomers* or *enantiomorphs*.

Since the optical activity was observed in solution, Pasteur concluded that the property was characteristic of molecules (and not of crystals). He proposed that like two sets of crystals (which were mirror images to each other), the molecules constituting the crystals were also mirror images of each other. Thus, the structures of optical isomers differ only in being mirror images of each other and their properties differ only in the direction of rotation of plane polarised light.

LeBel and Van't Hoff (1873) had proposed that the four valences of a carban atom are directed towards the four corners of a regular tetrahedron at the centre of which lies the carbon atom. A compound with four separate groups (*a*, *b*, *c* and *d*) attached to a carbon atom may be represented by the space models (Fig. 15.3). The two models look like mirror images of each other and are not superimposable. A tetrahedral model of fluorochlorobromomethane may thus be represented as shown in Fig. 15.4. Similarly, the two optically active isomeric forms of a compound like lactic acid or *sec*-butyl choloride may be represented as:

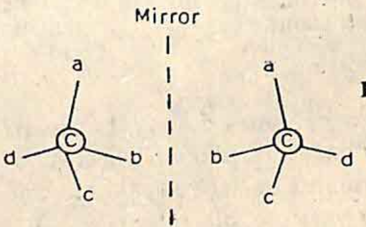


Fig. 15.3. Non-superimposable isomers.

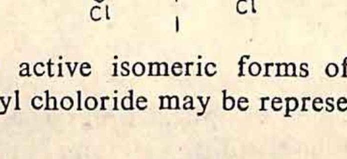
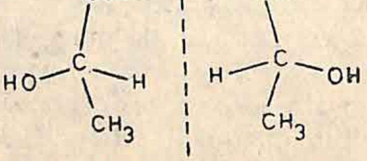
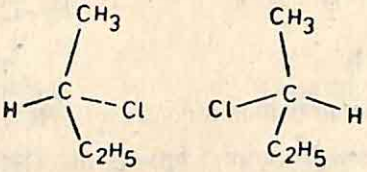


Fig. 15.4. Mirror image isomers of fluorochlorobromomethane.



(+) or *d*-Lactic acid (−) or *l*-Lactic acid

The form which rotates the plane of polarised light to right is dextro rotatory, i.e., *d*— or (+) form, and the other is laevo rotatory, i.e., *l*— or (−) form. Both the forms possess identical physical and chemical properties except for the direction of rotation of plane polarised light. An equimolar mixture of *d*– and *l*–isomers is optically inactive and is denoted as *dl* or (±) form. It is called ***racemic mixture*** or *modification*. This can be separated into *d*- and *l*- forms by suitable methods. The process of separation is known as *resolution*.



Enantiomers of *sec*-butyl chloride.

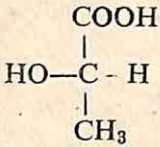
It is thus clear that the enantiomers are non-superimposable mirror images of each other. The non-superimposibilty arises because of the dissymmetric nature of the molecules. Thus we may say that a compound with dissymetric molecules can exist as enantiomers.

If we look at the examples of organic compounds which form enantiomers, we find that they contain a carbon atom which is attached to four different groups. Such a carbon atom which is attached to four different groups is called an *asymmetric carbon atom*. Most of the molecules, not all, which contain an asymmetric carbon are dissymetric. Compounds containing one asymmetric carbon atom are dissymmetric while those which contain more than one asymmetric carbon atom may or may not be dissymmetric. Thus optical activity is due to the dissymmetry of the molecules which in turn is due to the presence of at least one asymmetric carbon atom.

Configuration of Molecules

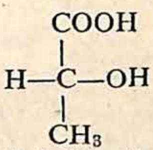
The spatial arrangement of substituents at an asymmetric carbon atom is known as the *configuration* of a molecule. In case of optical isomers, it is very important to determine their configurations.

Fischer has proposed a specific orientation in which an enantiomer molecule may be depicted. In this method, the molecule is held so that the asymmetric carbon of the molecule is in the plane of the paper. The groups at the top and bottom are inclined equally below the plane of paper while the groups on the right and left are inclined equally above the plane. These groups attached to the asymmetric carbon in the molecule are then projected to the plane in the form of a cross. The Fischer projection formulae for lactic acid may be depicted as:



$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ CH_3 \end{array}$$

L (+) Lactic acid



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ CH_3 \end{array}$$

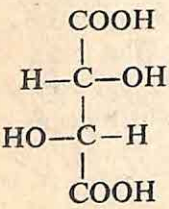
D (−) Lactic acid

Fischer projection formulae for lactic acid.

In these formulae, the isomer having the OH group on the right hand side is designated by the letter D while that having the OH on the left-hand side is designated by the letter L. The (+) and (—) signs stand for *dextro*-rotation and *laevo*-rotation, respectively. Thus L (+) lactic acid means *dextro* acid (*d*-form) with OH on the left-hand side while D (—) means *laevo* acid (*e*-form) with OH on the right-hand side. The D (+) and L (−), and D (—) and L (+) configurations are also possible in compounds containing more than one asymmetric carbon atoms.

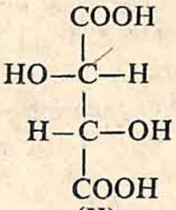
Molecules Containing Many Asymmetric Centres

Compounds containing more than one asymmetric carbon atom may exist in more than two stereoisomeric forms. Let us consider tartaric acid which contains two asymmetric carbon atoms. With the aid of the projection formulae, we can write the structures of various forms as:



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ COOH \end{array}$$

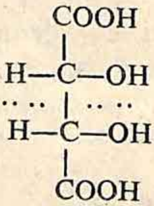
(I)



$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ COOH \end{array}$$

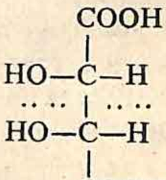
(II)

Non-superimposable enantiomers (*d*- and *l*-forms)



$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ \cdots\cdots | \cdots\cdots \\ H-C-OH \\ | \\ COOH \end{array}$$

(III)



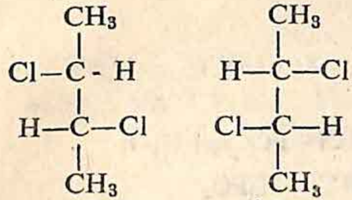
$$\begin{array}{c} COOH \\ | \\ HO-C-H \\ \cdots\cdots | \cdots\cdots \\ HO-C-H \\ | \\ COOH \end{array}$$

(IV)

Superimposable mirror images (represent *meso*-form)

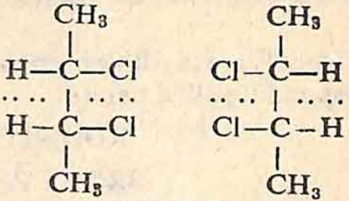
It can be seen that the structures (I) and (II) are non-superimposable mirror images and are thus enantiomers. The structures (III) and (IV) contain asymmetric carbon atoms but they are superimposable mirror images. They contain a plane of symmetry (shown by dotted line) and are known as *meso*-form. The *meso*-form is optically inactive since it has two identical carbon atoms whose optical activity counteracts and exactly balances each other.

2,3-Dichlorobutane provides another common example of a substance existing in three forms (a *d*-form, a *l*-form and a *meso* form).



d-form *l*-form

Non-superimposable enantiomers.



meso-form

Superimposable mirror images.

15.3. PREPARATION OF ALKYL HALIDES

Alkyl halides are prepared by the following methods:

1. From Alcohols

In this method, the hydroxyl group of an alcohol is replaced by a halogen. This may be accomplished by treating the alcohol with halogen acids, phosphorus halides or thionyl chloride.

WITH CONCENTRATED HALOGEN ACIDS

Alcohols react with concentrated halogen acids to give alkyl halides.

$$ROH + HX \longrightarrow RX + H_2O$$

The reactivities of halogen acids and alcohols follow the orders:

$$HI > HBr > HCl$$

Tertiary alcohol > secondary alcohol > primary alcohol

Alkyl chlorides are obtained by passing hydrogen chloride gas into alcohol in the presence of anhydrous zinc chloride. For example:

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + HCl \xrightarrow{ZnCl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + H_2O$$

Alkyl bromides and iodides are obtained by refluxing alcohol with excess of constant boiling HBr and HI, respectively. For example:

$$\underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} + HBr \longrightarrow \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2Br} + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + HI \longrightarrow \underset{\text{Ethyl iodide}}{CH_3CH_2I} + H_2O$$

Alkyl bromides can also be obtained by heating alcohol with sodium bromide or potassium bromide and concentrated sulphuric acid.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+KBr+H_2SO_4 \longrightarrow \underset{\text{Ethyl bromide}}{CH_3CH_2Br}+H_2O+KHSO_4$$

WITH PHOSPHORUS HALIDES

Alcohols react with phosphorus halides (PX_3 or PCl_5) to give corresponding alkyl halides.

$$ROH+PCl_5 \longrightarrow RCl+POCl_3+H_2O$$

$$3ROH+PX_3 \longrightarrow 3RCl+H_3PO_3$$

(where X=Cl, Br or I)

Alkyl chlorides are obtained by treating alcohols with PCl_3 or PCl_5. For example:

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+PCl_5 \longrightarrow \underset{\text{Ethyl chloride}}{CH_3CH_2Cl}+HCl+POCl_3$$

Alkyl bromides and iodides are obtained by the action of PBr_3 or PI_3 on alcohols. The trihalide is generated in the reaction by the action of bromine or iodine on phosphorus. For example:

$$\underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow[-H_3PO_3]{P/I_2} \underset{n\text{-Propyl iodide}}{CH_3CH_2CH_2I}$$

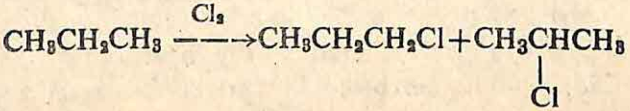
Alkyl chlorides are also obtained by the action of thionyl chloride on alcohols. This method is more convenient because both the by-products are gases and thus the purification is easy. For example:

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl}+SO_2+HCl$$

2. From Hydrocarbons

(i) DIRECT HALOGENATION

When alkanes are treated with halogens in presence of diffused sunlight and a catalyst, a mixture of alkyl halides is obtained. The separation of mixture into individual compounds is difficult. The method is generally used where the mixed alkyl halides are needed. For example:



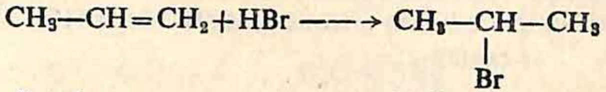
$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{Cl_2} \underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl}+\underset{\text{2-Chloropropane}}{CH_3\underset{\mid \atop Cl}{CH}CH_3}$$

(ii) WITH HYDROGEN HALIDES

Addition of hydrogen halide (HCl, HBr or HI) to an alkene gives an alkyl halide. For example:

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + HI \longrightarrow CH_3CH_2I$$

Unsymmetrical alkenes add hydrogen halides according to Markownikoff's rule. For example:



$$CH_3{-}CH{=}CH_2 + HBr \longrightarrow CH_3{-}\underset{\substack{|\\ Br}}{CH}{-}CH_3$$

Propylene *iso*-Propyl bromide

In the presence of bezoyl peroxide, HBr (not HCl or HI) gives 1-bromopropane as the major product. This is called *anti-Markownikoff's addition* (*peroxide effect* or *Kharasch effect*) because the resulting compound is different from that expected according to Markownikoff's rule.

$$\underset{\text{Propylene}}{CH_3{-}CH{=}CH_2} + HBr \longrightarrow \underset{\text{1-Bromopropane}}{CH_3{-}CH_2{-}CH_2Br}$$

3. By Halide Exchange

An alkyl iodide may be prepared from the corresponding bromide or chloride by treatment with a solution of sodium iodide in acetone. The less soluble sodium bromide or sodium chloride precipitates from solution and is filtered off. For example:

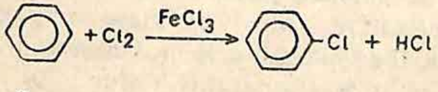
$$\underset{\text{Ethyl chloride}}{C_2H_5Cl} + NaI \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I} + NaCl$$

15.4. PREPARATION OF ARYL HALIDES

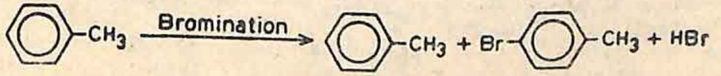
Aryl halides can be prepared by the following methods:

1. Direct Halogenation

Aryl chlorides and bromides are easily prepared by direct chlorination or bromination of an aromatic hydrocarbon at a low temperature, in absence of sunlight and in presence of a Lewis acid (like FeX_3 or AlX_3). For example:



Benzene Chlorobenzene

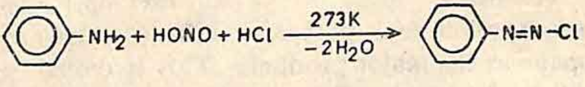


Toluene *o*-Bromotoluene *p*-Bromotoluene

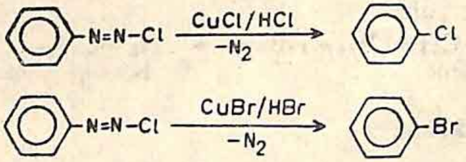
Alkyl fluorides and iodides cannot be obtained by this method.

2. From Diazonium Salts

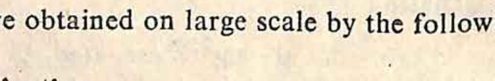
This is a very convenient method for preparing alkyl halides. The method consists in warming an aqueous solution of a diazonium salt with cuprous halide (CuCl or CuBr) dissolved in the corresponding halogen acid when the diazo group (—N=N—) is replaced by a halogen atom. The diazonium salt itself is obtained by treating an amino compound with nitrous acid ($NaNO_2+HCl$) at low temperature. For example:



Aniline Benzene diazonium chloride



Alkyl iodides are obtained by treating the diazonium salt with potassium iodide. For example:



Benzene diazonium chloride Iodobenzene

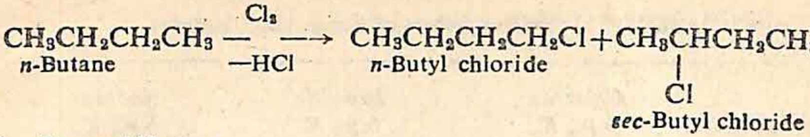
15.5. INDUSTRIAL PREPARATION

Alkyl halides are obtained on large scale by the following methods:

1. Direct Chlorination

Alkyl chlorides are prepared by direct chlorination of hydrocarbons at high temperature. The method yields a mixture of mono- and poly-substituted chloro derivative. Most of these compounds are used as industrial solvents, the separation is not necessary. However, they may be separated by fractional distillation. For example:

$$\underset{\text{Methane}}{CH_4} \xrightarrow[-HCl]{Cl_2} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow[-HCl]{Cl_2} \underset{\text{Methylene chloride}}{CH_2Cl_2} \xrightarrow[-HCl]{Cl_2} \underset{\text{Chloroform}}{CHCl_3} \xrightarrow[-HCl]{Cl_2} \underset{\text{Carbon tetrachloride}}{CCl_4}$$



$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[-HCl]{Cl_2} \underset{n\text{-Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} + \underset{sec\text{-Butyl chloride}}{CH_3\underset{\substack{|\\Cl}}{C}HCH_2CH_3}$$

2. From Alkynes

Some unsaturated alkyl halides which are used to prepare polymers can be obtained by addition of a halogen acid to an alkyne. For example:

$$\underset{\text{Acetylene}}{HC\equiv CH} + HCl \xrightarrow{HgCl_2} \underset{\text{Vinyl chloride}}{H_2C=CHCl}$$

15.6. PHYSICAL PROPERTIES

The lower members of alkyl halides (CH_3Cl, C_2H_5Cl and CH_3Br) are colourless gases at ordinary temperature while higher members are mostly pleasant smelling liquids. Members with very high molecular masses are solids.

The melting and boiling points of alkyl halides are higher than those of the corresponding alkanes because of the higher molecular masses of the halides. For a given alkyl group, the boiling points of the halides follow the order (Fig. 15.5, Table 15.1):

$$RCl < RBr < RI$$

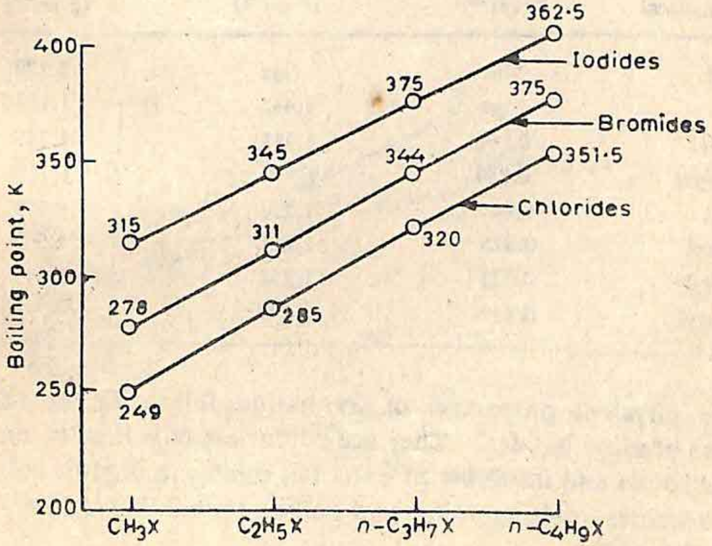


Fig. 15.5. Boiling points of alkyl halides.

TABLE 15.1: Boiling Points of Some Alkyl Halides

Alkyl radical	*Chloride b.p., K*	*Bromide b.p., K*	*Iodide b.p., K*
iso-Propyl	313.5	333.0	362.5
iso-Butyl	342.0	364.0	393.0
sec-Butyl	341.0	364.0	392.0
tert-Butyl	324.0	346.0	373.0

Because of their inability to form hydrogen bonds with water or to break the hydrogen bonds already existing in water, alkyl halides are insoluble in water. However, they are soluble in organic solvents.

Alkyl chlorides are generally lighter than water whereas bromides and iodides are heavier. Their densities follow the order (Table 15.2):

$$\mathrm{RCl} < \mathrm{RBr} < \mathrm{RI}$$

TABLE 15.2: Densities of Some Alkyl Halides

Alkyl radical	*Chloride (g cm⁻³)*	*Bromide (g cm⁻³)*	*Iodide (g cm⁻³)*
Methyl	Gas	Gas	2.279
Ethyl	Gas	1.440	1.933
n-Propyl	0.890	1.335	1.747
iso-Propyl	0.859	1.310	1.705
n-Butyl	0.884	1.276	1.617
iso-Butyl	0.875	1.261	1.605
sec-Butyl	0.871	1.258	1.595
tert-Butyl	0.840	1.222	——

The physical properties of aryl halides follow the same trends as those of alkyl halides. They are colourless oily liquids or crystalline solids and insoluble in water but soluble in organic solvents. Their densities, melting points and boiling points (Figs. 15.6–15.8) follow the order:

Chloro < bromo < iodo

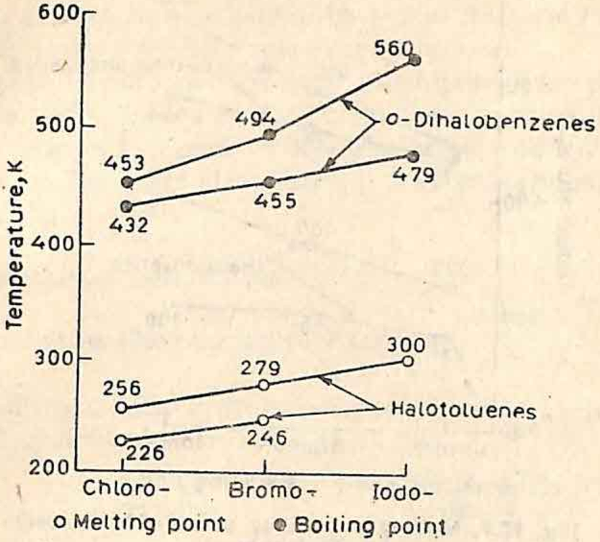


Fig. 15.6. Melting and boiling points of halotoluenes and *o*-dihalobenzenes.

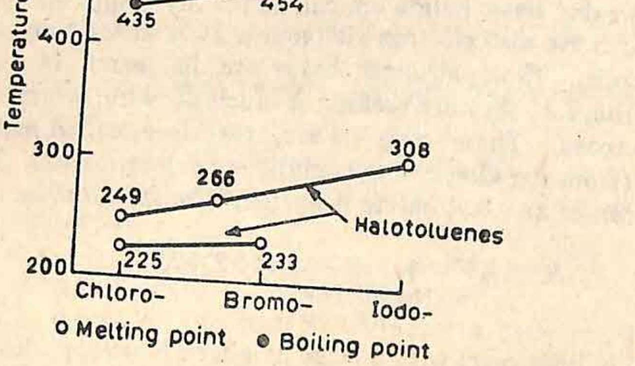


Fig. 15.7. Melting and boiling points of halotoluenes and *m*-dihalobenzenes.

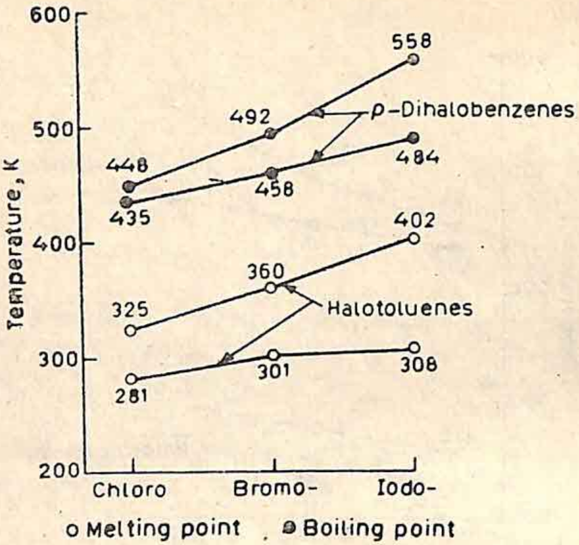
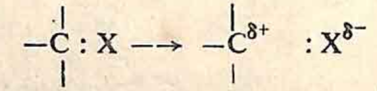


Fig. 15.8. Melting and boiling points of halotoluenes and *p*-dihalobenzenes.

15.7. CHEMICAL PROPERTIES

In alkyl halides, the halogen atom is attached to a carbon atom. As the halogen atom is more electronegative than carbon, the bond between carbon and halogen is slightly polar.



$$-\overset{|}{\underset{|}{C}}:X \longrightarrow -\overset{|}{\underset{|}{C}}{}^{\delta+}\quad :X^{\delta-}$$

The electron pair is nearer to the halogen atom, therefore, halide ion behaves as a Lewis base.

The weakly basic halide ion can be readily displaced by stronger bases which are also electron-rich and possess at least one lone pair of electrons. These stronger bases are in search of a relatively positive site, *i.e.*, they are seeking a nucleus with which to share their electrons. These reagents are, therefore, called ***nucleophilic reagents*** (from the Greek, nucleophilic = nucleus loving). The typical reaction of an alkyl halide is ***nucleophilic substitution.***

$$R^+:X^{\delta-} + \underset{\substack{\text{(Nucleophilic}\\ \text{reagent)}}}{:Z} \longrightarrow R:Z + X^-$$

Alkyl halides react with a large number of nucleophilic reagents, both organic and inorganic, to yield a wide variety of important products. These reagents include not only negative ions such as hydroxide (: OH^-), alkoxide (: OR^-) and cyanide (: CN^-), etc., but also neutral bases such as ammonia (: NH_3) and water (H_2O :) with the characteristic feature of having at least one unshared pair of electrons according to Lewis concept of bases.

Alkyl halides also undergo dehydrohalogenation to form alkynes and reduction to form alkanes. Further, they react with magnesium to form Grignard reagents which are of great synthetic importance in organic chemistry. Thus alkyl halides are very important from synthetic point of view.

1. Nucleophilic Substitution

(i HYDROLYSIS (PREPARTION OF ALCOHOLS)

Alkyl halides undergo hydrolysis on treatment with aqueous NaOH or KOH or moist silver oxide.

$$\underset{\text{Alkyl halide}}{RX} + K^+OH^- \longrightarrow \underset{\text{Alcohol}}{ROH} + KX$$

For example:

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + KOH \longrightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + KBr$$

(ii) WITH ALKOXIDES (PREPARATION OF ETHERS)

Alkyl halides react with sodium alkoxides forming ethers.

$$\underset{\text{Alkyl halide}}{RX} + \underset{\text{Sodim alkoxide}}{RO^-Na^+} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R} + NaX$$

For example:

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{Sodium ethoxide}}{C_2H_5ONa} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5{-}O{-}C_2H_5} + NaBr$$

(iii) WITH CYANIDES (PREPARATION OF ALKYL CYANIDES)

Alkyl halides react with alcoholic potassium cyanide to give alkyl cyanides.

$$\underset{\text{Alkyl halide}}{RX} + K^+CN^- \longrightarrow \underset{\text{Alkyl cyanide}}{R{-}C{\equiv}N} + KX$$

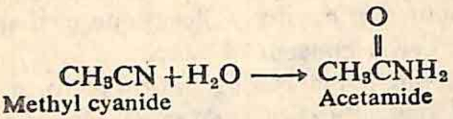
For example:

$$\underset{\text{Methyl iodide}}{CH_3I} + KCN \longrightarrow \underset{\text{Methyl cyanide}}{CH_3{-}C{\equiv}N} + KI$$

Alkyl cyanides on reduction with nascent hydrogen give primary amines. For example:

$$\underset{\text{Methyl cyanide}}{CH_3CN + 4H} \longrightarrow \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

Alkyl cyanides on partial hydrolysis give amides while on complete hydrolysis give carboxylic acids. For example:



$$\underset{\text{Methyl cyanide}}{CH_3CN + H_2O} \longrightarrow \underset{\text{Acetamide}}{CH_3\overset{\overset{O}{\|}}{C}NH_2}$$

$$\underset{\text{Methyl cyanide}}{CH_3CN + 2H_2O} \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

(iv) WITH SILVER CYANIDE (PREPARATION OF ISOCYANIDES)

Alkyl halides react with silver cyanide to give alkyl isocyanides as the main products.

$$\underset{\text{Alkyl halide}}{RX + Ag^+CN^-} \longrightarrow \underset{\text{Alkyl isocyanide}}{R-N\overset{\rightarrow}{=}C} + AgX$$

For example:

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + AgCN \longrightarrow \underset{\text{Ethyl isocyanide}}{C_2H_5N\overset{\rightarrow}{=}C} + AgBr$$

(v) WITH SILVER SALT OF A FATTY ACID (PREPARATION OF ESTERS)

Alkyl halides react with a silver salt of a fatty acid to give corresponding esters.

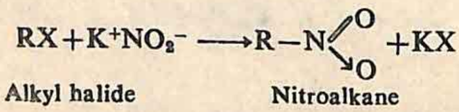
$$\underset{\text{Alkyl halide}}{RX} + \underset{\text{Silver salt of a fatty acid}}{R'\,COO^-Ag^+} \longrightarrow \underset{\text{Ester}}{R'COOR} + AgX$$

For example:

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{Silver acetate}}{CH_3COOAg} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + AgBr$$

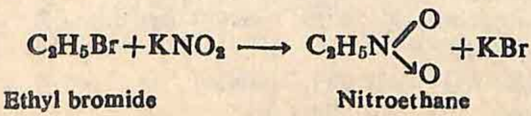
(vi) WITH POTASSIUM OR SODIUM NITRITE (PREPARATION OF NITROALKANES)

Alkyl halides react with potassium or sodium nitrite to yield nitroalkanes as the main products.



$$\underset{\text{Alkyl halide}}{RX + K^+NO_2^-} \longrightarrow \underset{\text{Nitroalkane}}{R-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}} + KX$$

For example:



$$\underset{\text{Ethyl bromide}}{C_2H_5Br + KNO_2} \longrightarrow \underset{\text{Nitroethane}}{C_2H_5N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}} + KBr$$

(vii) WITH SILVER NITRITE (PREPARATION OF ALKYL NITRITES)

When an alkyl halide reacts with silver nitrite, an alkyl nitrite is obtained as the chief product.

$$\underset{\text{Alkyl halide}}{RX} + Ag^+NO_2^- \longrightarrow \underset{\text{Alkyl nitrite}}{R-O-N=O} + AgX$$

For example

$$\underset{\text{Methyl iodide}}{CH_3I} + AgNO_2 \longrightarrow \underset{\text{Methyl nitrite}}{CH_3-O-N=O} + AgI$$

(viii) WITH SODIUM HYDROSULPHIDE (PREPARATION OF THIOALCOHOLS)

Thioalcohols are obtained when alkyl halides react with sodium hydrosulphide.

$$\underset{\text{Alkyl halide}}{RX} + Na^+SH^- \longrightarrow \underset{\text{Thioalcohol}}{RSH} + NaX$$

For example:

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + NaSH \longrightarrow \underset{\text{Ethyl thioalcohol}}{C_2H_5SH} + NaI$$

(ix) WITH SODIUM MERCAPTIDE (PREPARATION OF THIOETHERS)

Thioethers are obtained when alkyl halides react with sodium mercaptide.

$$\underset{\text{Alkyl halide}}{RX} + Na^+SR' \longrightarrow \underset{\text{Thioether}}{R-S-R'} + NaX$$

For example:

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + C_2H_5SNa \longrightarrow \underset{\text{Diethyl thioether}}{C_2H_5-S-C_2H_5} + NaBr$$

(x) WITH AMMONIA (PREPARATION OF AMINES)

Alkyl halides react with an alcoholic solution of ammonia to give a mixture of primary, secondary, and tertiary amines and quaternary ammonium salts. For example:

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + :NH_3 \longrightarrow \underset{\substack{\text{Ethylamine}\\\text{(primary)}}}{C_2H_5NH_2} + HI$$

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Ethylamine}}{:NH_2C_2H_5} \longrightarrow \underset{\substack{\text{Diethylamine}\\\text{(secondary)}}}{(C_2H_5)_2NH} + HI$$

$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Diethylamine}}{:NH(C_2H_5)_2} \longrightarrow \underset{\substack{\text{Triethylamine}\\\text{(tertiary)}}}{(C_2H_5)_3N} + HI$$

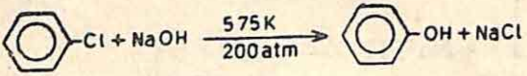
$$C_2H_5I + :N(C_2H_5)_3 \longrightarrow [(C_2H_5)_4N]^+I^-$$

Ethyl iodide Triethylamine Tetraethylammonium iodide (quaternary salt)

Aryl halides undergo nucleophilic substitution reactions only under drastic conditions. This is because the halogen atom is attached firmly to the nucleus and cannot be replaced easily. Some reactions given by aryl halides are:

(i) WITH SODIUM HYDROXIDE

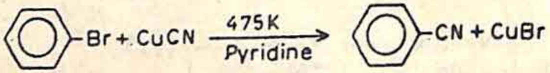
When an aryl halide is heated with concentrated sodium hydroxide solution at about 575K under high pressure, the halogen atom is replaced by a hydroxyl group. For example:



Chlorobenzene Phenol

(ii) WITH CUPROUS CYANIDE

On heating with cuprous cyanide at about 475K in the presence of pyridine, halogen atom of an aryl halide is replaced by —CN group. For example:

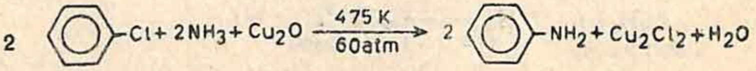


Bromobenzene

Cyanobenzene (phenyl cyanide)

(iii) WITH AMMONIA

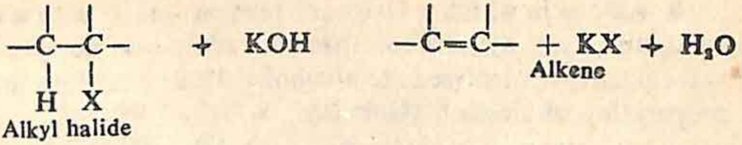
Halogen atom of an aryl halide is replaced by an amino group by treating it with aqueous ammonia at 475K, under 60 atmosphere pressure and in the presence of cuprous oxide catalyst. For example:



Chlorobenzene Aniline

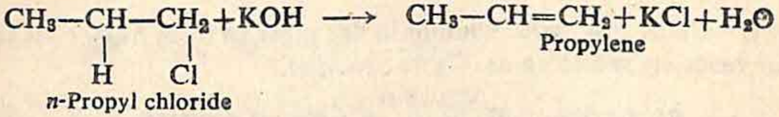
2. Dehydrohalogenation (Preparation of Alkenes)

Alkyl halides, when heated with alcoholic potassium hydroxide, get dehydrohalogenated and form alkenes.



$$\underset{\text{Alkyl halide}}{-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{X}{|}}{C}}-} + KOH \quad \underset{\text{Alkene}}{-\overset{|}{C}=\overset{|}{C}-} + KX + H_2O$$

For example:



$$\underset{n\text{-Propyl chloride}}{CH_3-\underset{\underset{H}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}} + KOH \longrightarrow \underset{\text{Propylene}}{CH_3-CH=CH_2} + KCl + H_2O$$

3. Reaction with Magnesium (Preparation of Grignard Reagents)

Alkyl halides (in diethyl ether) react with magnesium turnings to form organometallic compounds of the general formula, R—Mg —X. These compounds are known as *Grignard reagents* and are very useful to synthesize other compounds.

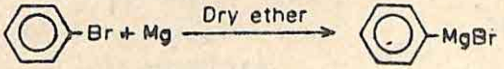
$$\underset{\text{Alkyl halide}}{RX} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

For example:

$$\underset{\text{Methyl bromide}}{CH_3Br + Mg} \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Methyl magnesium bromide}\\ \text{(Grignard reagent)}}}{CH_3MgBr}$$

$$\underset{\text{Ethyl iodide}}{C_2H_5I + Mg} \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Ethyl magnesium iodide}\\ \text{(Grignard reagent)}}}{C_2H_5MgI}$$

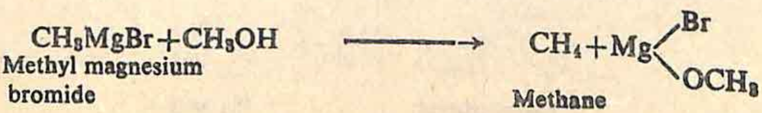
Aryl halides (bromides and iodides and not chlorides) and vinyl halides also form Grignard reagents but less readily. For example:



Bromobenzene Phenyl magnesium bromide (Grignard reagent)

Grignard reagents mainly give two types of reactions:

Reactions in which alkyl or aryl group of a Grignard reagent combines with active hydrogen of a compound like alcohol, acid, etc. For example:



$$\underset{\substack{\text{Methyl magnesium}\\ \text{bromide}}}{CH_3MgBr + CH_3OH} \longrightarrow \underset{\text{Methane}}{CH_4} + Mg\begin{matrix}\diagup Br\\ \diagdown OCH_3\end{matrix}$$

Reactions in which a Grignard reagent reacts with a compound containing carbonyl group, forms an additional compound and is subsequently hydrolysed to alcohol. These reactions are used in preparation of alcohols (Unit 16).

4. Reaction with Sodium

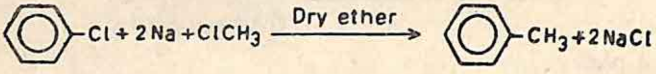
Alkyl halides react with sodium in dry ether to form higher alkanes. This reaction is known as *Wurtz reaction.*

$$\underset{\text{Alkyl halide}}{2RX+2Na} \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R{-}R}+2NaX$$

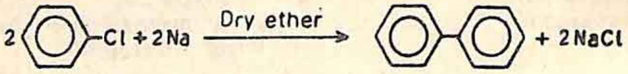
For example:

$$\underset{\text{Methyl bromide}}{2CH_3Br+2Na} \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3{-}CH_3}+2NaBr$$

The reaction in which both alkyl and aryl (or only aryl) halides are treated with sodium in dry ether is called *Wurtz-Fittig reaction* For example:



Chlorobenzene Methyl chloride Toluene



Chlorobenzene Diphenyl

5. Reduction

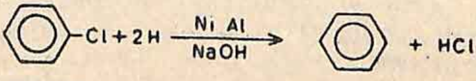
Alkyl halides are easily reduced to alkanes by reducing agents like nascent hydrogen (obtained from Zn+HCl, Zn+NaOH, etc.), hydrogen in presence of nickel catalyst, hydroiodic acid in presence of phosphorus, etc.

$$\underset{\text{Alkyl halide}}{RX+H_2} \xrightarrow[\text{Alkane}]{\text{Ni}} RH+HX$$

For example:

$$\underset{\text{Ethyl chloride}}{C_2H_5Cl+2H} \xrightarrow{\text{Zn+HCl}} \underset{\text{Ethane}}{C_2H_6}+HCl$$

An aryl halide is reduced to parent hydrocarbon by the action of nickel aluminium alloy in presence of an alkali. For example:



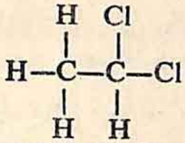
Chlorobenzene **Benzene**

15.8. POLYHALOGEN DERIVATIVES

Alkyl halides are monohalogen derivatives of hydrocarbons. In addition to these, we have halogen derivatives containing more than one halogen atoms per molecule. These are collectively known as ***polyhalogen derivatives***. We shall now deal with some dihalogen and trihalogen derivatives.

15.9. DIHALOGEN DERIVATIVES

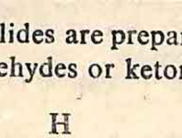
A dihalogen derivative is obtained by the replacement of two hydrogen atoms of an alkane by two halogen atoms. When both the halogen atoms are attached to the same carbon atom, the compounds are called *alkylidene halides*. This position of the substituents is called *geminal* position. For example, an alkylidene halide CH_3-CHCl_2 will be named as:



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-Cl$$

Ethylidene chloride or
1,1- dichloroethane or
geminal **or** ***gem*-dichloroethane**

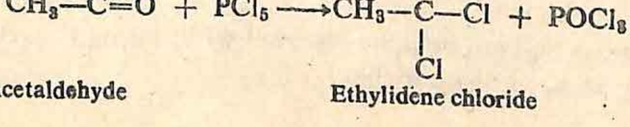
When the two halogen atoms are attached to *adjacent* carbon atoms, the compounds are called *alkylene halides*. This position of the substituents is known as *vicinal* position. For example, an alkylene halide CH_2Cl-CH_2Cl will be named as:



$$H-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Cl}{C}}-H$$

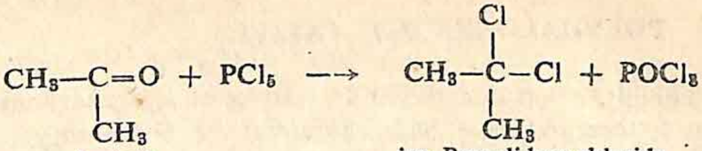
Ethylene chloride or
1,2-dichloroethane or
vicinal **or** ***vic*-dichloroethane**

Alkylidene halides are prepared by the action of phosphorus pentachloride on aldehydes or ketones. For example:



$$CH_3-\overset{H}{C}=O + PCl_5 \longrightarrow CH_3-\underset{Cl}{\overset{H}{C}}-Cl + POCl_3$$

Acetaldehyde **Ethylidene chloride**



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O + PCl_5 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}-Cl + POCl_3$$

Acetone iso- Propylidene chloride

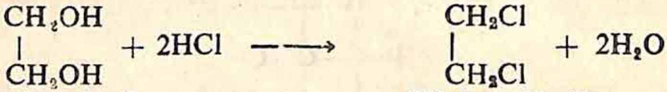
They are also obtained when halogen acids react with acetylenes. For example:

$$\underset{\text{Acetylene}}{CH\equiv CH} + HBr \longrightarrow \underset{\text{Vinyl bromide}}{CH_2=CHBr} \xrightarrow{+HBr} \underset{\text{Ethylidene bromide}}{CH_3-CHBr_2}$$

Alkylene halides are prepared by the addition of halogens to olefins. For example:

$$\underset{\text{Ethylene}}{CH_2=CH_2} + Cl_2 \longrightarrow \underset{\text{Ethylene chloride}}{CH_2Cl-CH_2Cl}$$

They can also be obtained by the action of halogen acids on glycols. For example:



$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 2HCl \longrightarrow \begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} + 2H_2O$$

Ethylene glycol Ethylene chloride

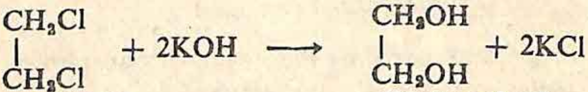
Ethylidene chloride boils at 330K and ethylene chloride boils at 357K. Some important reactions of the two classes of compounds are:

(i) Reaction with Aqueous Potassium Hydroxide

On hydrolysis with aqueous potassium hydroxide, alkylidene halides give aldehydes or ketones. For example:

$$\underset{\text{Ethylidene chloride}}{CH_3CHCl_2+2KOH} \xrightarrow[-2KCl]{} \underset{\text{(Unstable)}}{CH_3CH(OH)_2} \xrightarrow[-H_2O]{} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Under similar conditions of hydrolyis, alkylene halides form glycols. For example:

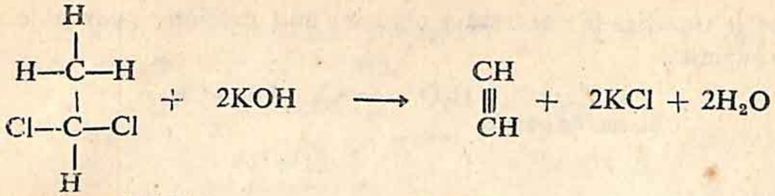


$$\begin{matrix}CH_2Cl\\|\\CH_2Cl\end{matrix} + 2KOH \longrightarrow \begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix} + 2KCl$$

Ethylene chloride Ethylene glycol

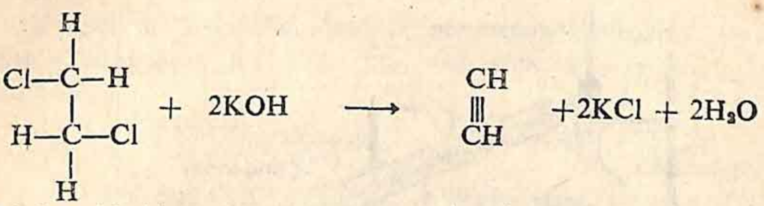
(ii) Reaction with Alcoholic Potassium Hydroxide

Both the types of compounds react with alcoholic potash and give acetylenes. For example:



$$\mathrm{H{-}\overset{H}{\underset{|}{\overset{|}{C}}}{-}H \;\; Cl{-}\underset{H}{\overset{|}{\underset{|}{C}}}{-}Cl} + 2KOH \longrightarrow \mathrm{CH{\equiv}CH} + 2KCl + 2H_2O$$

Ethylidene chloride Acetylene



$$\mathrm{Cl{-}\overset{H}{\underset{|}{\overset{|}{C}}}{-}H \;\; H{-}\underset{H}{\overset{|}{\underset{|}{C}}}{-}Cl} + 2KOH \longrightarrow \mathrm{CH{\equiv}CH} + 2KCl + 2H_2O$$

Ethylene chloride Acetylene

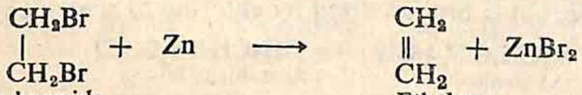
(iii) **Reaction with Zinc**

Alkylidene halides react with zinc to form olefins containing double the number of carbon atoms. For example:

$$2CH_3CHBr_2 + 2Zn \longrightarrow CH_3CH{=}CHCH_3 + 2ZnBr_2$$

Ethylidene bromide β—Butylene

Alkylene halides react with zinc to give olefins containing the same number of carbon atoms. For example:



$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + Zn \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ZnBr_2$$

Ethylene bromide Ethylene

15.10. TRIHALOGEN DERIVATIVES

A trihalogen derivative is obtained by replacement of three hydrogen atoms of an alkane by three halogen atoms. The trihalogen derivatives of methane are:

	$CHCl_3$	$CHBr_3$	CHI_3
Common name :	Chloroform	Bromoform	Iodoform
IUPAC name :	Trichloromethane	Tribromomethane	Triiodomethane

They are collectively known as *haloforms.*

Chloroform

In the laboratory or on a large scale, chloroform is prepared by distilling ethyl alcohol or acetone with bleaching powder. Bleaching powder supplies the necessary chlorine and calcium hydroxide for the reaction.

$$\underset{\text{Bleaching powder}}{CaOCl_2} + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

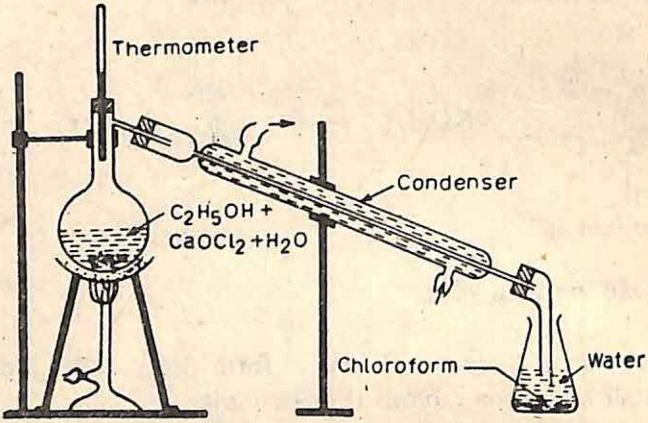


Fig. 15.9. Laboratory preparation of chloroform.

The reaction with ethyl alcohol may be represented by the following steps:

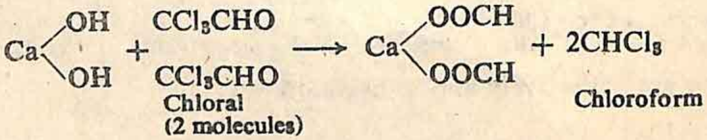
(*i*) Ethyl alcohol is first oxidized by chlorine to acetaldehyde.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + Cl_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + 2HCl$$

(*ii*) Acetaldehyde reacts with more of chlorine to give trichloroacetaldehyde or chloral.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

(*iii*) Chloral so obtained is hydrolysed by calcium hydroxide (obtained from bleaching powder) when it gives chloroform and calcium formate.



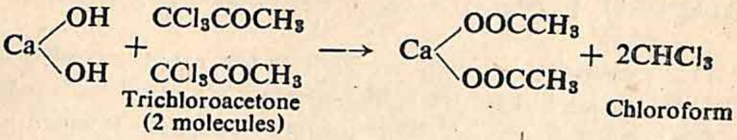
$$Ca\begin{matrix} OH \\ OH \end{matrix} + \underset{\substack{\text{Chloral} \\ \text{(2 molecules)}}}{\begin{matrix} CCl_3CHO \\ CCl_3CHO \end{matrix}} \longrightarrow Ca\begin{matrix} OOCH \\ OOCH \end{matrix} + \underset{\text{Chloroform}}{2CHCl_3}$$

In case of acetone, the reaction may be represented as:

(*i*) Acetone gets chlorinated to form trichloroacetone.

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3COCH_3} + 3HCl$$

(*ii*) Trichloroacetone reacts with calcium hydroxide and gives chloroform and calcium acetate.



$$Ca\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} + \underset{\substack{\text{Trichloroacetone}\\ \text{(2 molecules)}}}{\begin{matrix}CCl_3COCH_3\\ CCl_3COCH_3\end{matrix}} \longrightarrow Ca\begin{matrix}\diagup OOCCH_3\\ \diagdown OOCCH_3\end{matrix} + \underset{\text{Chloroform}}{2CHCl_3}$$

Pure chloroform of anaesthetic grade can be obtained by distilling chloral or chloral hydrate with aqueous sodium hydroxide solution.

$$NaOH+\underset{\text{Chloral}}{CCl_3CHO} \longrightarrow HCOONa+\underset{\text{Chloroform}}{CHCl_3}$$

$$NaOH+\underset{\text{Chloral hydrate}}{CCl_3CH(OH)_2} \longrightarrow HCOONa+\underset{\text{Chloroform}}{CHCl_3}+H_2O$$

It is a colourless, heavy liquid which has a sweet odour and taste. It boils at 334K and is slightly soluble in water.

In presence of light, it is oxidized by air and the product obtained is a poisonous compound, carbonyl chloride or phosgene.

$$\underset{\text{Chloroform}}{2CHCl_3}+O_2 \xrightarrow{\text{Light}} \underset{\substack{\text{Carbonyl chloride}\\ \text{(phosgene)}}}{2COCl_2}+2HCl$$

Chloroform is used as an anaesthetic and in medicines. It is a good solvent for resins, fats and waxes. It is used as a laboratory reagent and also as a preservative for anatomical specimens.

Iodoform

Iodoform is prepared by the action of iodine and alkali on ethyl alcohol or acetone. The reaction may be represented as:

(*i*) *With alcohol*

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH}+I_2 \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}+2HI$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO}+3I_2 \longrightarrow \underset{\text{Triiodoacetaldehyde}}{CI_3CHO}+3HI$$

$$NaOH+\underset{\text{Triiodoacetadehyde}}{I_3CCHO} \longrightarrow \underset{\text{Iodoform}}{CHI_3}+HCOONa$$

(*ii*) *With acetone*

$$\underset{\text{Acetone}}{CH_3COCH_3}+3I_2 \longrightarrow \underset{\text{Triiodoacetone}}{CI_3COCH_3}+3HI$$

$$NaOH+\underset{\text{Triiodoacetone}}{I_3CCOCH_3} \longrightarrow \underset{\text{Iodoform}}{CHI_3}+CH_3COONa$$

In the laboratory, it is generally prepared by using sodium carbonate in place of sodium hydroxide.

$$C_2H_5OH+4I_2+3Na_2CO_3 \rightarrow 5NaI+HCOONa+3CO_2+2H_2O+\underset{\text{Iodoform}}{CHI_3}$$

This reaction is used as a test for ethyl alcohol, acetadehyde and all such ketones which contain a methyl group attached to the carbonyl group. The test substance is warmed at about 335K with a dilute solution of sodium carbonate and iodine. The appearance of characteristic yellow precipitate of iodoform which has a distinct smell shows the presence of any of the above compounds. The test is known as *iodoform test*.

EXERCISES

15.1 What is meant by isomerism? What are the different types of isomerism?

15.2 Give the different forms of structural isomerism, giving examples in each case.

15.3 What is stereoisomerism ? What are its types?

15.4 Write a note on geometrical isomerism.

15.5 What is plane polarised light? How is it obtained?

15.6 What is meant by optical activity?

15.7 Explain the following terms:
(*i*) Enantiomerism (*ii*) Racemic mixture
(*iii*) Asymmetric carbon atom (*iv*) Configuration

15.8 Explain optical isomerism shown by organic compounds.

15.9 Give examples of compounds containing two asymmetric carbon atoms.

15.10 Write Fischer projection formulae and explain their significance.

15.11 Give the general methods of preparation of alkyl halides.

15.12 Alkyl halides are the compounds of great synthetic importance. Discuss.

15.13 What are trihalogen compounds and haloforms?

15.14 How will you prepare chloroform from (*i*) ethyl alcohol and (*ii*) acetone?

15.15 What is iodoform test?

15.16 Starting from ethyl bromide, how will you obtain the following:
(*i*) Ethyl alcohol (*ii*) Ethane (*iii*) Diethyl ether
(*iv*) Propionic acid (*v*) Ethylamine (*vi*) Ethyl acetate

15.17 What are aryl halides? Give methods for the preparation of chlorobenzene.

15.18 How does chlorobenzene react with
(*i*) NaOH (*ii*) NH_3 (*iii*) CuCN

15.19 How will you convert benzene into chlorobenzene and vice versa?

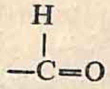
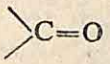
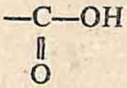
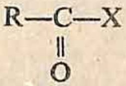
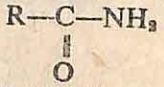
15.20 Write notes on: (*i*) Wurtz reaction (*ii*) Wurtz-Fittig reaction.

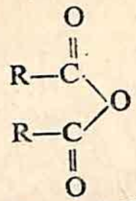
Unit 16

Compounds with Functional Groups Containing Oxygen

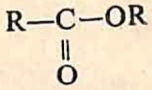
Alcohols, Phenols and Ethers: Nomenclature, General methods of preparation and properties, Hydrogen bonding, Industrial uses. Aldehydes and Ketones: Nature of the carbonyl group, Nomenclature, Preparation and properties. Carboxylic acids. Derivatives of carboxylic acids: Acid halides, amides and anhydrides.

In this Unit, we shall study organic compounds which contain oxygen in their functional groups. The main classes of such compounds and their functional groups are:

Class of compounds	*Functional group*	
Alcohols and phenols	$-OH$	
Ethers	$-O-$	
Aldehydes	 $-\overset{\text{H}}{\overset{\mid}{C}}=O$	
Ketones	 $>C=O$	
Carboxylic acids	 $-\underset{\underset{O}{\Vert}}{C}-OH$	
Acid derivaties	 $R-\underset{\underset{O}{\Vert}}{C}-X$ Acid halides	 $R-\underset{\underset{O}{\Vert}}{C}-NH_2$ Acid amides



Acid anhydrides



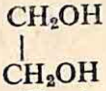
$R{-}\overset{\displaystyle O}{\underset{}{C}}{-}OR$ (with $=O$ below C)

Esters

16.1. ALCOHOLS AND PHENOLS

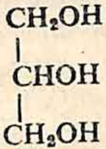
The compounds containing one or more hydroxyl groups (—OH) are called *alcohols* or *phenols*. An alcohol contains the —OH group attached to an alkyl group while in a phenol, the group is attached to an aromatic ring. The compounds are classified as *mono-*, *di-* and *trihydric* alcohols or phenols according to the number of —OH groups contained in their molecules. Thus:

CH_3CH_2OH
Ethyl alcohol
(Monohydric)



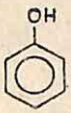
$CH_2OH{-}CH_2OH$

Glycol
(Dihydric)

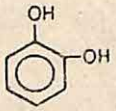


$CH_2OH{-}CHOH{-}CH_2OH$

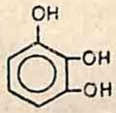
Glycerol
(Trihydric)



Phenol
(Monohydric)



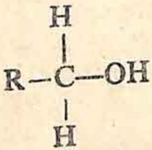
Catechol
(Dihydric)



Pyrogallol
(Trihydric)

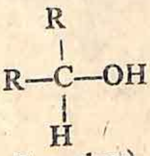
When four or more hydroxyl groups are present, they are called *polyhydric* alcohols or phenols.

Monohydric alcohols are further classified as *primary*, *secondary* or *tertiary* alcohols according to the hydroxyl group is attached to a primary, secondary or tertiary carbon atom.



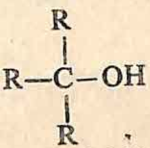
$R{-}\underset{H}{\overset{H}{C}}{-}OH$

(Primary)



$R{-}\underset{H}{\overset{R}{C}}{-}OH$

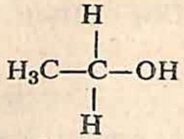
(Secondary)



$R{-}\underset{R}{\overset{R}{C}}{-}OH$

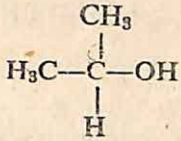
(Tertiary)

For example:



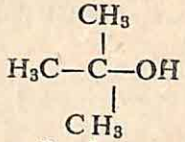
$H_3C{-}\overset{H}{\underset{H}{C}}{-}OH$

Ethyl alcohol
(Primary)



$H_3C{-}\overset{CH_3}{\underset{H}{C}}{-}OH$

iso-Propyl alcohol
(Secondary)

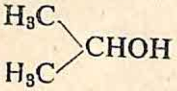


$H_3C{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH$

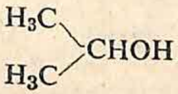
tert-Butyl alcohol
(Tertiary)

16.2. NOMENCLATURE

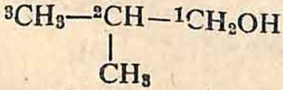
There are two main systems of naming alcohols. In the *common system*, the name of the compound is derived by adding the word alcohol after the name of the alkyl radical present in the molecule. Thus:

CH_3OH	Methyl alcohol
CH_3CH_2OH	Ethyl alcohol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol
	*iso*-Propyl alcohol

In the *IUPAC system*, alcohols are named as alkanols and the name of a particular alcohol is derived by substituting the terminal 'e' of the parent alkane by 'ol'. Thus:

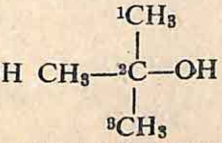
CH_3OH	Methanol
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2OH$	1-Propanol
	2-Propanol

For naming higher alcohols, the longest chain of carbon atoms containing the —OH group is selected as the parent chain. The positions of the —OH group and the side chains are indicated by numbers in such a way that the carbon with the —OH group gets the lowest possible number. For example:



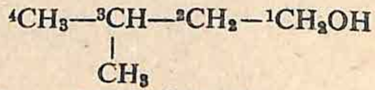
$^{3}CH_3{-}^{2}\underset{CH_3}{CH}{-}^{1}CH_2OH$

2-Methyl-1-propanol



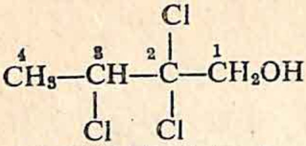
$CH_3{-}^{2}\overset{^{1}CH_3}{\underset{^{3}CH_3}{C}}{-}OH$

2-Methyl-2-propanol



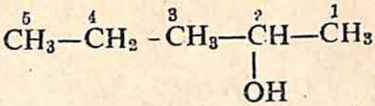
$^{4}CH_3{-}^{3}\underset{CH_3}{CH}{-}^{2}CH_2{-}^{1}CH_2OH$

3-Methylbutanol



$$\overset{4}{C}H_3-\underset{Cl}{\overset{3}{C}H}-\underset{Cl}{\overset{Cl}{\overset{2}{C}}}-\overset{1}{C}H_2OH$$

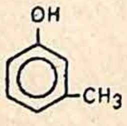
2, 2, 3-Trichlorobutanol



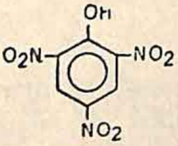
$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\underset{OH}{\overset{2}{C}H}-\overset{1}{C}H_3$$

2-Pentanol

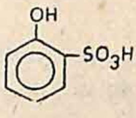
Phenols are named as the derivatives of the simplest aromatic hydroxy compound, phenol. Methylphenols are known as cresols.



m-Cresol



2,4,6-Trinitrophenol



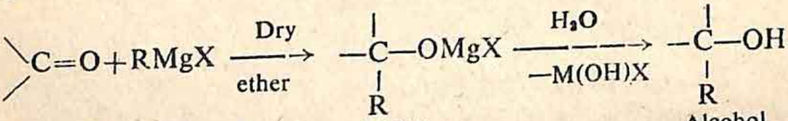
o-Phenolsulphonic acid

16.3. GENERAL METHODS OF PREPARATION

Alcohols

1. FROM ALDEHYDES AND KETONES

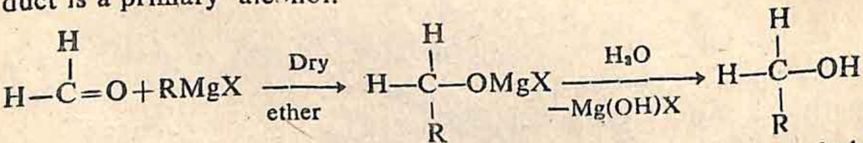
(*a*) By Grignard reagent (RMgX): This is a very important method for preparing primary, secondary and tertiary alcohols. The general reaction may be shown as:



$$>C=O+RMgX \xrightarrow[ether]{Dry} -\underset{R}{\overset{|}{C}}-OMgX \xrightarrow[-M(OH)X]{H_2O} -\underset{R}{\overset{|}{C}}-OH$$

Carbonyl compound Grignard reagent Addition product Alcohol

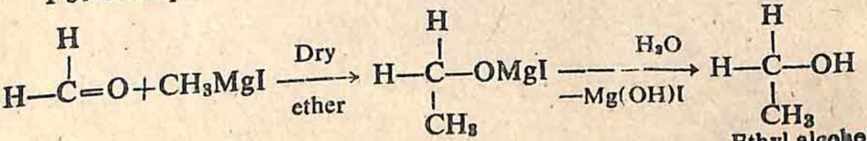
If the carbonyl compound used is formaldehyde, the final product is a primary alcohol.



$$H-\overset{H}{C}=O+RMgX \xrightarrow[ether]{Dry} H-\underset{R}{\overset{H}{C}}-OMgX \xrightarrow[-Mg(OH)X]{H_2O} H-\underset{R}{\overset{H}{C}}-OH$$

Formaldehyde Addition product Primary alcohol

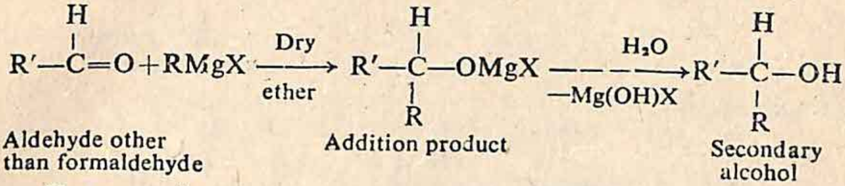
For example:



$$H-\overset{H}{C}=O+CH_3MgI \xrightarrow[ether]{Dry} H-\underset{CH_3}{\overset{H}{C}}-OMgI \xrightarrow[-Mg(OH)I]{H_2O} H-\underset{CH_3}{\overset{H}{C}}-OH$$

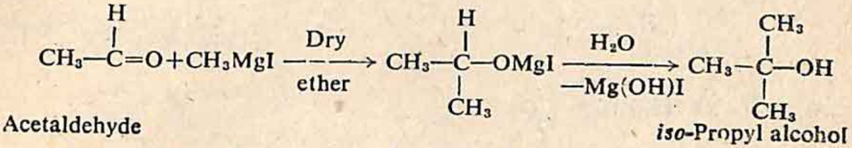
Formaldehyde Ethyl alcohol

If the carbonyl compound used is some aldehyde except formaldehyde, the final product is a secondary alcohol.



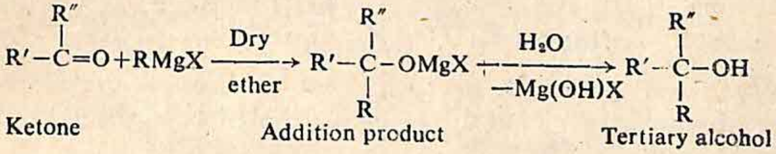
$$R'-\overset{H}{C}=O+RMgX \xrightarrow[\text{ether}]{\text{Dry}} R'-\overset{H}{\underset{R}{C}}-OMgX \xrightarrow[-Mg(OH)X]{H_2O} R'-\overset{H}{\underset{R}{C}}-OH$$

For example:



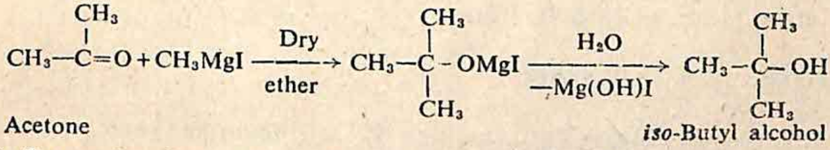
$$CH_3-\overset{H}{C}=O+CH_3MgI \xrightarrow[\text{ether}]{\text{Dry}} CH_3-\overset{H}{\underset{CH_3}{C}}-OMgI \xrightarrow[-Mg(OH)I]{H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

If the carbonyl compound used is a ketone, the final product is a tertiary alcohol.



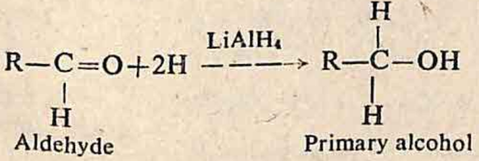
$$R'-\overset{R''}{C}=O+RMgX \xrightarrow[\text{ether}]{\text{Dry}} R'-\overset{R''}{\underset{R}{C}}-OMgX \xrightarrow[-Mg(OH)X]{H_2O} R'-\overset{R''}{\underset{R}{C}}-OH$$

For example:



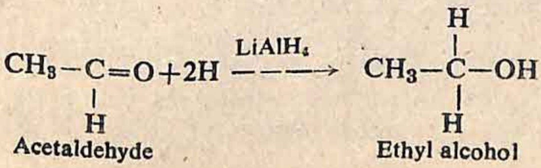
$$CH_3-\overset{CH_3}{C}=O+CH_3MgI \xrightarrow[\text{ether}]{\text{Dry}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OMgI \xrightarrow[-Mg(OH)I]{H_2O} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

(b) **By reduction of carbonyl compounds:** Carbonyl group ($>C=O$) containing aldehydes and ketones can be reduced to primary and secondary alcohols respectively. The commonly used reducing agents are $LiAlH_4$ (in ethereal solution), sodium and ethanol, and hydrogen in presence of a catalyst like Ni, Pd or Pt.

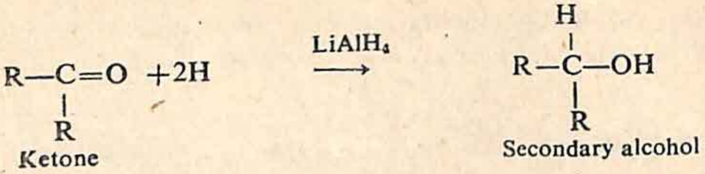


$$R-\underset{H}{C}=O+2H \xrightarrow{LiAlH_4} R-\overset{H}{\underset{H}{C}}-OH$$

For example:

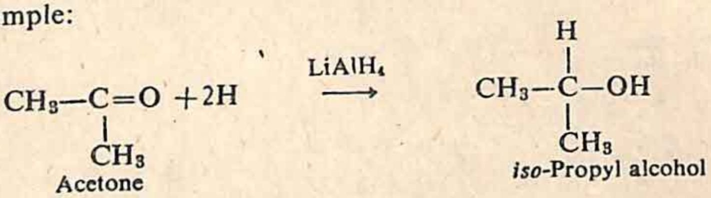


$$CH_3-\underset{H}{C}=O+2H \xrightarrow{LiAlH_4} CH_3-\overset{H}{\underset{H}{C}}-OH$$



$$\underset{\text{Ketone}}{\mathrm{R{-}\underset{\underset{\displaystyle R}{|}}{C}{=}O}} + 2\mathrm{H} \xrightarrow{\mathrm{LiAlH_4}} \underset{\text{Secondary alcohol}}{\mathrm{R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}{-}OH}}$$

For example:



$$\underset{\text{Acetone}}{\mathrm{CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}O}} + 2\mathrm{H} \xrightarrow{\mathrm{LiAlH_4}} \underset{\textit{iso}\text{-Propyl alcohol}}{\mathrm{CH_3{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}OH}}$$

FROM ALKYL HALIDES

The hydrolysis of alkyl halides with an aqueous alkali or moist silver oxide yields alcohols. Thus:

$$\underset{\text{Alkyl halide}}{\mathrm{RX}} + \underset{\text{(Aqueous)}}{\mathrm{KOH}} \longrightarrow \underset{\text{Alcohol}}{\mathrm{ROH}} + \mathrm{KX}$$

For example:

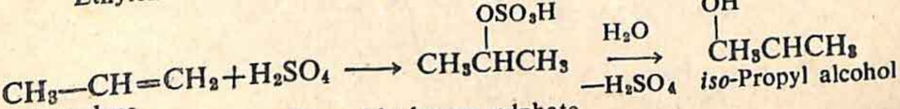
$$\underset{\text{Ethyl bromide}}{\mathrm{C_2H_5Br}} + \underset{\text{(Aqueous)}}{\mathrm{KOH}} \longrightarrow \underset{\text{Ethyl alcohol}}{\mathrm{C_2H_5OH}} + \mathrm{KBr}$$

Industrially alcohols are prepared by hydration of alkenes and fermentation of carbohydrates.

HYDRATION OF ALKENES

Alkenes are obtained by cracking of petroleum and are separated from the mixture by fractionation. When passed through sulphuric acid, they are absorbed giving alkyl hydrogen sulphate. The product when boiled with water gives alcohols. For example:

$$\underset{\text{Ethylene}}{\mathrm{CH_2{=}CH_2}} + \mathrm{H_2SO_4} \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{\mathrm{CH_3CH_2HSO_4}} \xrightarrow[-\mathrm{H_2SO_4}]{\mathrm{H_2O}} \underset{\text{Ethyl alcohol}}{\mathrm{CH_3CH_2OH}}$$



$$\underset{\text{Propylene}}{\mathrm{CH_3{-}CH{=}CH_2}} + \mathrm{H_2SO_4} \longrightarrow \underset{\textit{iso-}\text{ Propyl hydrogen sulphate}}{\mathrm{CH_3\overset{\overset{\displaystyle OSO_3H}{|}}{C}HCH_3}} \xrightarrow[-\mathrm{H_2SO_4}]{\mathrm{H_2O}} \underset{\textit{iso}\text{-Propyl alcohol}}{\mathrm{\overset{\overset{\displaystyle OH}{|}}{C}H_3CHCH_3}}$$

FERMENTATION OF CARBOHYDRATES

Fermentation is the process of degradation of organic compounds by certain complex nitrogenous substances called *enzymes* which are present in yeast and other micro-organisms. This is the oldest method for the manufacture of ethyl alcohol. The carbohydrate used is either sugar or some starchy material like rice, barley, maize or potatoes. The reactions taking place with sugar and starch are:

FROM SUGAR

$$\underset{\text{Sucrose}}{C_{12}H_{12}O_{11}} + H_2O \xrightarrow[\text{(yeast)}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow[\text{(yeast)}]{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

FROM STARCH

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)n} + nH_2O \xrightarrow[\text{(yeast)}]{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(yeast)}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

The enzymes *invertase*, *zymase* and *maltase* are present in yeast while the enzyme *diastase* is obtained by the germination of barley.

Methyl alcohol is obtained as a by-product during the destructive distillation of wood in closed retorts out of contact with air. It is also manufactured from water gas (a mixture of $CO+H_2$). The gas is mixed with hydrogen and passed over a catalyst (mixture of oxides of copper, zinc and chromium) at 625-675K.

$$CO + 2H_2 \xrightarrow[\text{(catalyst)}]{\text{625-675K}} CH_3OH$$

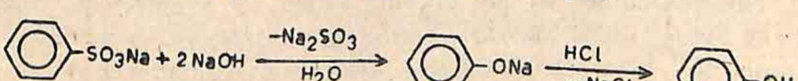
PHENOLS

1. FROM COAL TAR

Phenols and cresols are recovered from the middle fraction (443-503K) obtained on the distillation of coal tar.

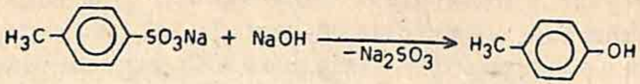
2. ALKALI FUSION OF SULPHONATES

Phenols are obtained by fusion of aromatic sulphonates with sodium hydroxide followed by acidification. For example:



Sodium benzene sulphonate

Phenol

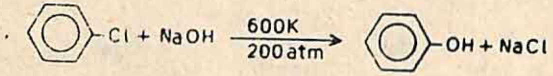


Sodium-*p*-toluenesulphonate

p-Cresol

3. From Alkyl Halides (Dow's process)

Phenol is obtained on a large scale by heating chlorobenzene with 10% NaOH solution at about 600K and under a pressure of 200 atmospheres in the presence of a copper catalyst.



Chlorobenzene

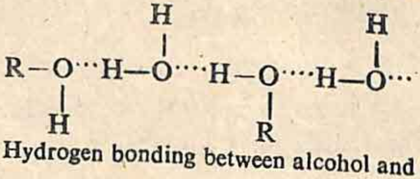
Phenol

16.4. PHYSICAL PROPERTIES

Alcohols are composed of a non-polar hydrocarbon part and the polar —OH group. The properties are a combined effect of these two components.

The lower alcohols are colourless volatile liquids with a characteristic alcoholic smell and a burning taste. The higher members are colourless solids.

The first three members are completely miscible with water. The solubility rapidly decreases with the increasing number of carbon atoms. The highest members are practically insoluble in water. The solubility of lower alcohols is because of hydrogen bonding with water. The rapid fall in solubility of higher alcohols is due to the fact that the large repulsive effect of non-polar portion of alcohol outweighs the solubility effect of—OH group. The higher alcohols are soluble in organic solvents.

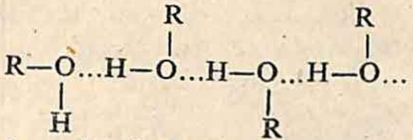


$$\mathrm{R{-}\underset{\substack{|\\H}}{O}\cdots H{-}\overset{\substack{H\\|}}{O}\cdots H{-}\underset{\substack{|\\R}}{O}\cdots H{-}\overset{\substack{H\\|}}{O}\cdots}$$

Hydrogen bonding between alcohol and water

The specific gravity and boiling points of alcohols increase as the molecular mass increases. Amongst themselves, a primary alcohol has a higher boiling point than the corresponding secondary alcohol and the latter has a higher boiling point than the corresponding tertiary alcohol. The higher boiling point of an alcohol compared to the corresponding hydrocarbon and alkyl halides (as given below) is because of hydrogen bonding amongst alcohols.

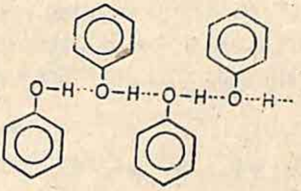
Compound:	CH_4	CH_3Cl	CH_3Br	CH_3OH
Boiling point, K:	111	249	278	337.5



$$R-\underset{H}{O}\cdots H-\overset{R}{O}\cdots H-\underset{R}{O}\cdots H-\overset{R}{O}\cdots$$

Hydrogen bonding amongst alcohols

Phenols also boil at a higher temperature compared to corresponding hydrocarbons (e.g., phenol boils at 455K and toluene at 384K) because of intermolecular hydrogen bonding.



Intermolecular hydrogen bonding in phenol

Phenol itself and some di- and trihydric phenols are fairly soluble in water but most other phenols are insoluble because of the dominant hydrocarbon part in the molecule.

16.5. CHEMICAL PROPERTIES

Chemical reactions of alcohols may be studied under two heads:

(1) Involving cleavage of O—H bond and

(2) Involving cleavage of C—O bond.

1. Reactions Involving the Cleavage of Oxygen-Hydrogen (O⋮H) Bond

(i) ACID CHARACTER

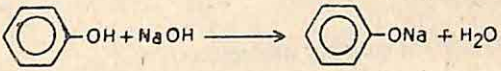
Alcohols react with active metals such as sodium, potassium and magnesium to form metal alkoxides, RO^-M^+.

$$\underset{\text{Alcohol}}{ROH}+Na \longrightarrow \underset{\text{Sodium alkoxide}}{RO^-Na^+ + \tfrac{1}{2}H_2}$$

For example:

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH}+2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5ONa} + H_2$$

This suggests that alcohols act as weak acids (weaker than even water). This is because of the polarized O—H bond which allows the separation of H^+ ion. The acid character decreases as we move from a primary to secondary to tertiary alcohol because of increasing number of alkyl groups. Compared to alcohols, phenols are more acidic and readily form *phenoxides* with an aqueous alkali.



Phenol Sodium phenoxide

(ii) ESTERIFICATION

Alcohols and phenols react with organic acids to form *esters*. The process is called *esterification*. It is carried out in the presence of a dehydrating agent such as concentrated sulphuric acid or dry hydrogen chloride.

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{RCOOR'} + H_2O$$

For example:

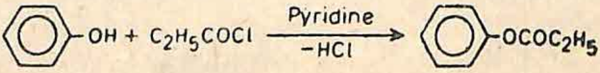
$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

(iii) ACYLATION

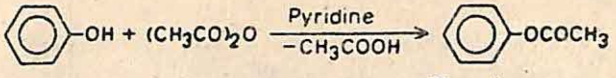
When an alcohol or a phenol is treated with an acid choloride or acid anhydride, it results in the formation of an ester. The process is known as *acylation* and takes place more rapidly than esterification with acid. It is carried on in presence of a base (such as pyridine) which removes the acid formed during the reaction. For example:

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + C_2H_5OH \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + C_2H_5OH \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$



Phenol Phenyl propionate



Phenol Phenyl acetate

(iv) OXIDATION

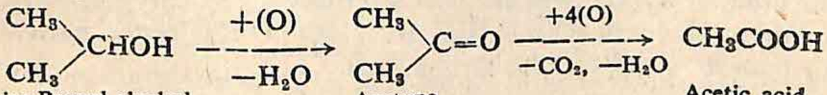
Alcohols can be oxidized by various oxidizing agents such as potassium permanganate (in acidic, alkaline or neutral medium), acidified dichromate solution or dilute nitric acid. The ease of oxidation and the nature of the product formed depend on the type of alcohol used.

A primary alcohol on oxidation first gives an *aldehyde* and then an acid, both containing the same number of carbon atoms as the original alcohol. For example:

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[-H_2O]{+(O)} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[-H_2O]{+(O)} \underset{\text{Acetic acid}}{CH_3COOH}$$

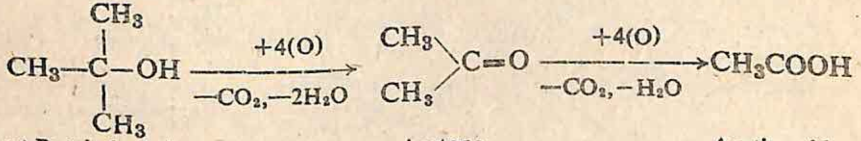
The reaction can be stopped at the aldehyde stage by using a suitable oxidizing agent and distilling away the product as soon as it is formed.

A secondary alcohol on oxidation gives a *ketone* with the same number of carbon atoms as the original alcohol. The ketone on further drastic oxidation gives an acid with fewer carbon atoms than the original alcohol. For example:



iso-Propyl alcohol Acetone Acetic acid

Tertiary alcohols are resistant to oxidation in neutral or alkaline medium. However, they are oxidized by acid oxidizing agents to a mixture of ketone and acid each containing fewer carbon atoms than the original alcohol. For example:



tert-Butyl alcohol Acetone Acetic acid

(v) REACTION WITH GRIGNARD REAGENT

Alcohols react with Grignard reagent to produce hydrocarbons.

$$\underset{\text{Alcohol}}{ROH}+\underset{\substack{\text{Grignard}\\ \text{reagent}}}{R'MgX} \longrightarrow \underset{\text{Hydrocarbon}}{R'H}+ROMgX$$

For example:

$$\underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Ethyl magnesium iodide}}{C_2H_5MgI} \longrightarrow \underset{\text{Ethane}}{C_2H_6} + CH_3OMgI$$

2. Reactions Involving the Cleavage of Carbon-Oxygen (C—O) Bond

(i) REACTION WITH MINERAL ACIDS

We have seen that alcohols act as weak acids in their reactions with active metals. They can also behave as weak bases because of the lone pairs of electrons on the oxygen atom. Thus, in presence of a strong acid (halogen acid, sulphuric acid, etc.), they become protonated.

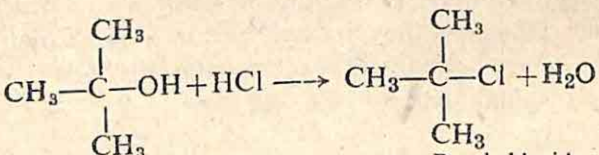
$$\underset{\text{Alcohol}}{R{-}\ddot{\underset{..}{O}}H} + HX \rightleftharpoons \underset{\text{Protonated alcohol}}{R{-}\overset{+}{\underset{..}{O}}H_2}$$

The positive charge on the oxygen atom weakens the C—O bond and we obtain:

$$R{-}OH_2 \rightleftharpoons R^+ + H_2O$$
$$R^+ + X^- \longrightarrow \underset{\text{Alkyl halide}}{RX}$$

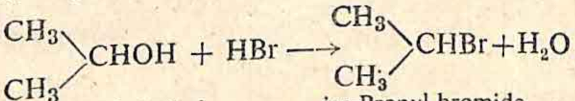
The order of reactivity of alcohols is tertiary > secondary > primary and that of halogen acids is HI > HBr > HCl (I^- is a better nucleophile than Br^- and Br^- is better than Cl^-).

For example:



$$CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OH + HCl \longrightarrow CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}Cl + H_2O$$

tert-Butyl alcohol *tert*-Butyl chloride



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHOH + HBr \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHBr + H_2O$$

iso-Propyl alcohol *iso*-Propyl bromide

The presence of anhydrous zinc chloride (dehydrating agent) enables the reaction to go to completion by removing water formed.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + HCl \xrightarrow[-H_2O]{\text{Anhydrous } ZnCl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl}$$

(ii) DEHYDRATION

Alcohols undergo dehydration when heated with a dehydrating acid such as sulphuric acid or phosporic acid, or their vapours are passed over heated alumina at 625K. For example:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{H_2SO_4,\ 443K} \underset{\text{Ethylene}}{CH_2{=}CH_2}$$

The case of dehydration follows the order:

tertiary>secondary>primary

In the reaction between an alcohol and sulphuric acid, different products may be obtained depending on the reaction conditions. For example, ethyl alcohol reacts with sulphuric acid at 383 K to give ethyl hydrogen sulphate. The product can be distilled under reduced pressure to obtain diethyl sulphate.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH+H_2SO_4} \xrightarrow{383K} \underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5HSO_4} + H_2O$$

$$\underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{2C_2H_5HSO_4} \longrightarrow \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4}+H_2SO_4$$

Also, when heated to 413K in the presence of more of ethyl alcohol, it gives ether.

$$\underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5HSO_4}+C_2H_5OH \xrightarrow{413K} \underset{\text{Ether}}{C_2H_5OC_2H_5}+H_2SO_4$$

When heated to 433-443K, in the presence of more of H_2SO_4, it is changed to ethylene.

$$\underset{\substack{\text{Ethyl hydrogen}\\\text{sulphate}}}{C_2H_5HSO_4} \xrightarrow{433\text{-}443K} \underset{\text{Ethylene}}{C_2H_4}+H_2SO_4$$

(iii) REACTION WITH PHOSPHORUS HALIDES OR THIONYL HALIDES

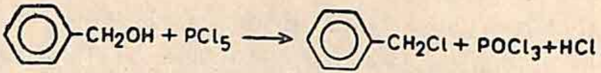
Alcohols react with phosphorus halides (PX_5 or PX_3) or thionyl halides to give corresponding halides.

$$\underset{\text{Alcohol}}{ROH}+PX_5 \longrightarrow \underset{\text{Alkyl halide}}{RX}+POX_3+HX$$

$$\underset{\text{Alcohol}}{3ROH}+PX_3 \longrightarrow \underset{\text{Alkyl halide}}{3RX}+H_3PO_3$$

$$\underset{\text{Alcohol}}{ROH}+SOX_2 \longrightarrow \underset{\text{Alkyl halide}}{RX}+SO_2+HX$$

For example:



Benzyl alcohol Benzyl chloride

$$\underset{\text{Ethyl alcohol}}{3C_2H_5OH}+PBr_3 \longrightarrow \underset{\text{Ethyl bromide}}{3C_2H_5Br}+H_3PO_3$$

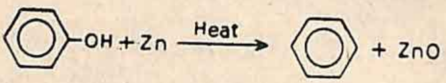
$$\underset{\text{Ethyl alcohol}}{C_2H_5OH}+SOCl_2 \longrightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl}+SO_2+HCl$$

Reactions of Phenols

Phenols are very reactive compounds and undergo reactions of the phenolic --OH group as well as those in which the ring substitution takes place. We have already considered some reactions of the former type. Two more such reactions may be mentioned.

REACTION WITH ZINC DUST

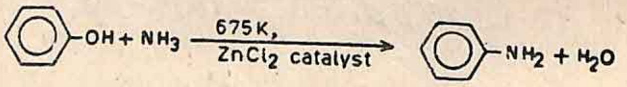
On distilling with zinc dust, phenols form corresponding aromatic hydrocarbons. For example:



Phenol Benzene

REACTION WITH AMMONIA

On heating with ammonia at high temperature and pressure, and in presence of anhydrous zinc chloride catalyst, —OH group of phenols undergoes replacement by —NH_2 group. For example:



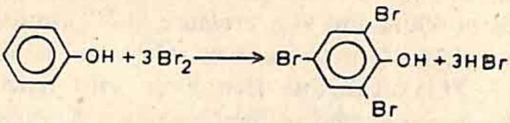
Phenol Aniline

Ring Substitution Reactions

The phenolic —OH group activates the ring to electrophilic substitution and thus acts as *ortho*- and *para*-directing. Some important ring substitution reactions are given below:

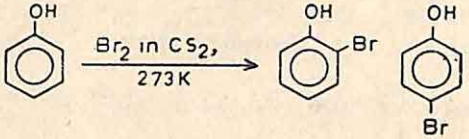
HALOGENATION

Phenols readily react with halogens to form polyhalogen substituted compounds. For example, phenol gives white precipitate of 2,4,6-tribromophenol when treated with bromine water.



Phenol 2,4,6-Tribromophenol

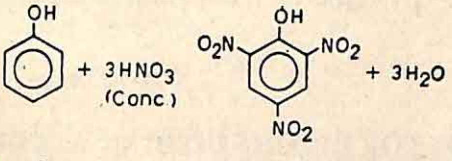
Monobromophenol is obtained by reacting phenol with bromine in the presence of less polar solvent such as carbon disulphide or carbon tetrachloride at low temperature.



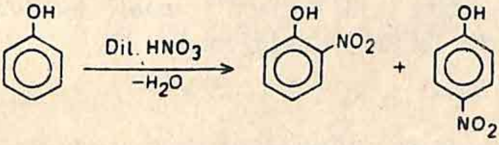
Phenol *o*-Bromophenol *p*-Bromophenol

NITRATION

Phenol forms 2,4,6-trinitrophenol (picric acid) with concentrated nitric acid and yields a mixture of *ortho*- and *para*-nitrophenols with dilute nitric acid at low temperature.



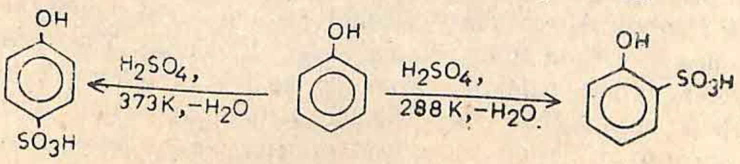
Phenol 2,4,6-Trinitrophenol



Phenol *o*-Nitrophenol *p*-Nitrophenol

SULPHONATION

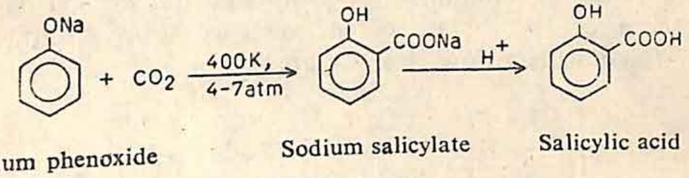
Sulphuric acid sulphonates the phenol chiefly to *ortho*-isomer at low temperature and to *para*-isomer at high temperature.



p-Phenolsulphonic acid Phenol *o*-Phenolsulphonic acid

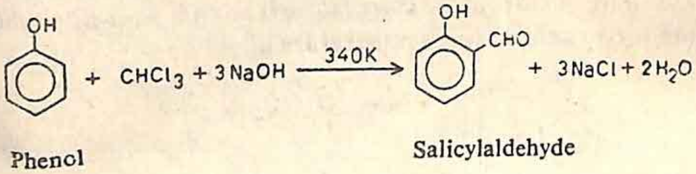
KOLBE'S REACTION

When sodium salt of phenol (sodium phenoxide) is heated with carbon dioxide at 400K and at a pressure of 4-7 atmosphere, sodium salt of *o*-hydroxybenzoic acid (sodium salicylate) is obtained as the main product. This on further treatment with hydrochloric acid yields *o*-hydroxybenzoic acid (salicylic acid). A small amount of *p*-isomer is also obtained.



REIMER-TIEMANN REACTION

When heated with chloroform and aqueous alkali, phenols form phenolic aldehydes (mainly the *ortho*-isomer). This is known as *Reimer-Tiemann reaction*. For example:



16.6. METHODS FOR DISTINGUISHING ALCOHOLS

Primary, secondary and tertiary alcohols may be distinguished from one another by the following methods.

(i) Oxidation Test

The mode of oxidation of three types of alcohols is characteristic for each type. The identification of the products of oxidation of a given alcohol indicates whether it is a primary, secondary or tertiary alcohol. A primary alcohol forms an aldehyde and then an acid containing the same number of carbon atoms as the original alcohol. A secondary alcohol gives a ketone with the same number of carbon atoms as the original alcohol. The ketone on further drastic oxidation gives an acid with a lesser number of carbon atoms than the original alcohol. A tertiary alcohol is resistant to oxidation in neutral or alkaline medium. With acid oxidizing agent, it gives a mixture of a ketone and carboxylic acid each containing a lesser number of carbon atoms than the original alcohol.

(ii) Lucas Test

In this test, an alcohol is treated with an equimolar mixture of concentrated hydrochloric acid and anhydrous zinc chloride (Lucas reagent). The alcohol reacts to form the corresponding alkyl chloride which is indicated by the appearance of cloudiness in the reaction mixture. A tertiary alcohol reacts immediately, a secondary alcohol reacts within a few minutes while a primary alcohol does not react at room temperature and hence no cloudiness is observed in this case.

(iii) Reaction with Hot Reduced Copper

When the vapours of alcohols are passed over reduced copper at 575K, primary and secondary alcohols are dehydrogenated to to aldehydes and ketones, respectively. Tertiary alcohols lose water and form alkenes.

16.7. TESTS FOR PHENOLS

Phenols are usually insoluble in water and aqueous sodium bicarbonate solution. However, their dissolution in aqueous sodium hydroxide solution serves as a test.

Phenols form characteristic coloured complexes (blue, green, red or violet) with neutral ferric chloride solution. This is an important test for phenolic —OH group and is not given by alcohols.

16.8. ABSOLUTE ALCOHOL

Absolute (or anhydrous) alcohol is 100% pure ethyl alcohol. When aqueous alcohol is fractionally distilled, rectified spirit containing a maximum of 95% alcohol is obtained. It is not possible to obtain more concentrated alcohol from rectified spirit by fractional distillation because ethyl alcohol and water form a constant boiling mixture (351.15K) containing 95.6% alcohol. However, repeated distillation of rectified spirit over quicklime gives alcohol which contains about 0.3% water. The last traces of water are eliminated by distilling over a calculated amount of sodium or calcium.

Absolute alcohol is produced on a large scale by *azeotropic distillation*. In this process, rectified spirit is mixed with some benzene and the mixture is distilled. At first, a ternary mixture containing all the water (7.4%), benzene (74.1%) and alcohol (18.5%) distills over at 337.85K. It is then followed by a binary mixture of benzene (67.6%) and alcohol (32.4%) at 341.3K. Finally 100% pure ethyl alcohol passes over at 351.3K).

16.9. INDUSTRIAL ALCOHOL

Ethyl alcohol is of immense value in industry. It is also highly intoxicating agent and used in alcoholic beverages. Alcohol needed for industry is available at much cheaper rates but it is highly taxed for its use in beverages. To make alcohol unfit for drinking purposes, it is mixed with poisonous substances like methyl alcohol, acetone, pyridine or gasoline. The process is called *denaturing* and the product is known as *methylated spirit* or *denatured alcohol*. Mixed with petrol hydrocarbons, ethyl alcohol is also used as a fuel in automobiles. It is then called *power alcohol*.

16.10. TOXICITY OF ALCOHOLS

Some alcohols are toxic in nature. The toxicity varies from alcohol to alcohol. Methyl alcohol is highly toxic—even a small amount taken internally may cause blindness or may prove to be fatal. Ethyl alcohol, though non-toxic, but slows down the functioning of brain and produces physiological effects.

16.11. USES OF ALCOHOLS AND PHENOLS

Alcohols and phenols are used for a variety of purposes. Some important uses of methyl alcohol, ethyl alcohol and phenol are given below.

Methyl alcohol is used:

(i) As a solvent for plastics, paints, varnishes, etc.

(ii) In the production of formaldehyde, an important material for the manufacture of plastics.

(iii) As an antifreeze in engine radiators.

(iv) As a power booster in gasoline engines. Airliners burn a carburettor injection mixture of 60% methyl alcohol.

(v) For denaturing ethyl alcohol.

Ethyl alcohol is used:

(i) As a solvent for drugs, tinctures, gums, varnishes, lacquers, oils, cosmetics, perfumes, dyes, inks, etc.

(ii) As a beverage.

(iii) As a preservative in biological specimens.
(iv) As an antifreeze in automobile radiators.
(v) In sterilizing surgical instruments.
(vi) In the manufacture of organic compounds like chloroform, iodoform, ether, acetic acid, etc.
(vii) As methylated spirit and as power alcohol.
(viii) As a fuel in lamps and stoves.

Phenol is used:

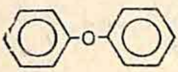
(i) In production of bakelite plastics.
(ii) As a powerful antiseptic in soaps, lotions, etc.
(iii) For preparing dyes, perfumes, local anaesthetics, etc.
(iv) In the manufacture of drugs like salol, salicylic acid, aspirin, etc.
(v) In the manufacture of picric acid, used as an explosive and as a dye.

16.12. ETHERS

Ethers are a class of organic compounds having the general formula R-O-R′ (where R and R′ may be alkyl or aryl groups). If R and R′ are alike, the ether is said to be a *simple* or *symmetrical* ether. For example:

CH_3-O-CH_3

Dimethyl ether

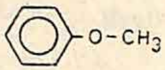


Diphenyl ether

In case R and R′ are different, it is called a *mixed* or *unsymmetrical* ether. For example:

CH_3-O-C_2H_5

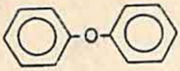
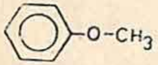
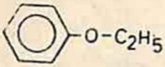
Methyl ethyl ether



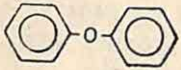
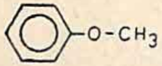
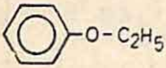
Methyl phenyl ether

16.13. NOMENCLATURE

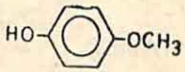
There are two systems of naming ethers. In the *common system*, the names of the members are derived by adding the word ether after the names of the alkyl radicals linked to the oxygen atom. In case of mixed ethers, the two radicals are named in order of increasing weight. Thus:

CH_3-O-CH_3	Dimethyl ether or methyl ether
C_2H_5-O-C_2H_5	Diethyl ether or ethyl ether
	Diphenyl ether or phenyl ether
$CH_3-O-C_2H_5$	Methyl ethyl ether
	Methyl phenyl ether
	Ethyl phenyl ether

In the *IUPAC system*, ethers are considered to be the alkoxy (—OR) derivatives of alkanes. In case of a mixed ether, the higher alkyl radical determines the name of the parent compound while the lower for the alkoxy group. Thus:

$CH_3—O-CH_3$	Methoxymethane
$C_2H_5-O-C_2H_5$	Ethoxyethane
	Phenoxybenzene
$CH_3—O-C_2H_5$	Methoxyethane
	Methoxybenzene
	Ethoxybenzene

When an —OH group is also present in the ether molecule, the compound is treated as the derivative of the alcohol and the ether group is named as an alkoxy substitute. For example:

$CH_3OCH_2CH_2OH$	
2-Methoxyethanol	*p*-Methoxyphenol

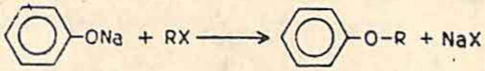
Some ethers are better known by special names. For example, methoxybenzene and ethoxybenzene are popularly known as anisole and phenetole, respectively.

16.14. GENERAL METHODS OF PREPARATION OE ETHERS

(1) Both symmetrical and unsymmetrical types of ethers are

generally prepared by heating alkyl halides with appropriate alkoxides or phenoxides. The method is known as *Williamson synthesis*.

$$\underset{\text{Sodium alkoxide}}{RONa} + \underset{\text{Alkyl halide}}{R'X} \longrightarrow \underset{\text{Ether}}{ROR' + NaX}$$

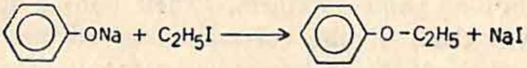


Sodium phenoxide Ether

For example :

$$\underset{\text{Sodium ethoxide}}{C_2H_5\,ONa + C_2H_5\,I} \longrightarrow \underset{\text{Diethyl ether}}{C_2H_5{-}O{-}C_2H_5 + NaI}$$

$$\underset{\text{Sodium ethoxide}}{C_2H_5\,ONa + CH_3Br} \longrightarrow \underset{\text{Methoyl ethyl ether}}{C_2H_5{-}O{-}CH_3 + NaBr}$$



Sodium phenoxide Phenetole

(2) Alcohols can be dehydrated to ethers by heating them with concentrated sulphuric acid (or galacial phosphoric acid). It is necessary to regulate the temperature and use an excess of alcohol to avoid the formation of alkenes.

$$2ROH \xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} R{-}O{-}R$$

$$\underset{\text{Ethyl alcohol}}{2C_2H_5OH} \xrightarrow[413K]{\text{Conc. } H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5{-}O{-}C_2H_5 + H_2O}$$

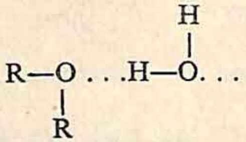
The above method is generally employed for the large-scale production of diethyl ether. A mixture of the two reactants in equimolar proportion is heated by superheated steam (temperature maintained at 413K) when ether distills over.

Ether free from moisture and alcohol (known as *absolute ether*) is obtained by the distillation of ordinary ether from concentrated sulphuric acid. It is stored over metallic sodium.

16.15. PHYSICAL PROPERTIES OF ETHERS

Dimethyl ether and methyl ethyl ether are gases at ordinary temperature but most ethers are colourless, volatile and pleasant smelling liquids. They are highly inflammable and lighter than water.

Ethers are freely soluble in alcohols and other common organic solvents. They behave as very good solvents themselves. Their solubility in water is comparable to that of isomeric alcohols. For example, about 8 g each of diethyl ether and isomeric *n*-butyl alcohol are soluble per 100 g of water. The solubility of ethers is probably because of some hydrogen bonding between water and ether molecules.



$$R{-}\underset{\substack{|\\ R}}{O}\cdots H{-}\overset{\substack{H\\ |}}{O}\cdots$$

Hydrogen bonding between ether and water

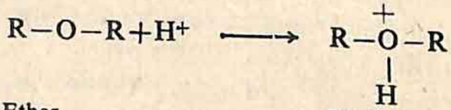
Ethers possess an angular structure with C—O—C bond angle of about 110°. Thus, they are weakly polar and show dipole moments of 1.2 to 1.3 D. However, this weak polarity does not affect the boiling points of ethers. Their boiling points are comparable with those of the corresponding alkanes but are much lower than those of the corresponding alcohols. This is due to the lack of hydrogen bonding in ether molecules.

16.16. CHEMICAL PROPERTIES OF ETHERS

Ethers are relatively inert and stable compounds and are used as solvents for many reactions. They are not attacked by dilute acids, alkalies, oxidizing agents and reducing agents. However, they give the following reactions:

Formation of Oxonium Salts

Due to the presence of the free electron pairs on the oxygen atom, ethers behave as weak bases and form oxonium salts with strong mineral acids.

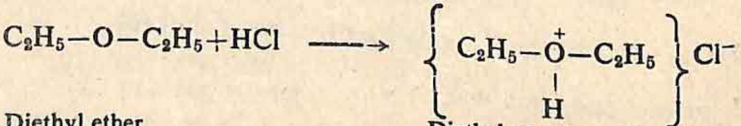


$$R{-}O{-}R + H^+ \longrightarrow R{-}\underset{\substack{|\\ H}}{\overset{+}{O}}{-}R$$

Ether

Dialkyl oxonium salt

For example:



$$C_2H_5{-}O{-}C_2H_5 + HCl \longrightarrow \left\{ C_2H_5{-}\underset{\substack{|\\ H}}{\overset{+}{O}}{-}C_2H_5 \right\} Cl^-$$

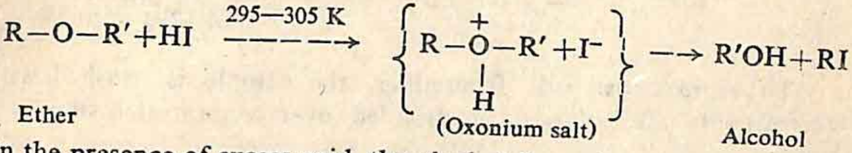
Diethyl ether

Diethyl oxonium chloride

The salts are stable only in presence of strong acids and at low temperature. They are decomposed back to the ether and the acid in aqueous medium.

Cleavage

When an ether is heated with a concentrated halogen acid, particularly hydroiodic acid, the molecule undergoes cleavage and the alkyl group is separated from the alkoxy group.

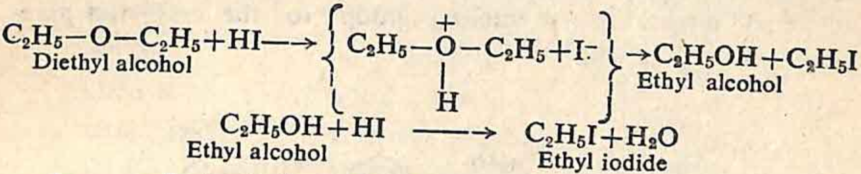


$$\underset{\text{Ether}}{R-O-R'+HI} \xrightarrow{295-305\text{ K}} \underset{\text{(Oxonium salt)}}{\left\{ R-\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}-R'+I^- \right\}} \longrightarrow \underset{\text{Alcohol}}{R'OH+RI}$$

In the presence of excess acid, the alcohol formed reacts further to give alkyl halide.

$$R'OH+HI \longrightarrow R'I+H_2O$$

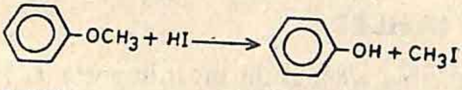
For example:



$$\underset{\text{Diethyl alcohol}}{C_2H_5-O-C_2H_5+HI} \longrightarrow \left\{ C_2H_5-\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}-C_2H_5+I^- \right\} \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH}+C_2H_5I$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH+HI} \longrightarrow \underset{\text{Ethyl iodide}}{C_2H_5I+H_2O}$$

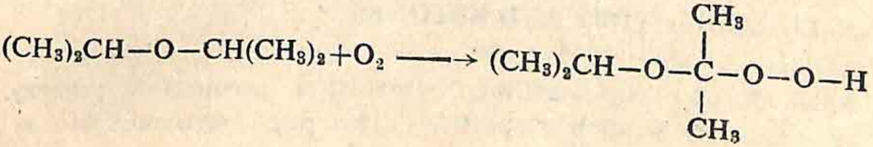
In case of mixed ethers, the cleavage of *aromatic* C—O bond is more difficult than that of the *alkyl* C—O bond. The cleavage of such ethers results in the formation of a phenol and an alkyl halide. For example:



Anisole Phenol

Peroxide Formation

Ethers are not affected by oxidizing agents such as potassium permanganate and potassium dichromate but on prolonged contact with air or ozone, they form peroxides. These are unstable and liable to explode.



$$(CH_3)_2CH-O-CH(CH_3)_2+O_2 \longrightarrow (CH_3)_2CH-O-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-O-O-H$$

The old samples of ethers may contain peroxides. These should be removed before distilling the ethers.

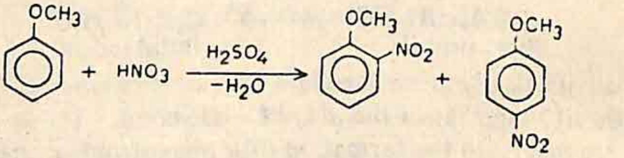
To detect the presence of peroxide in an ether, the sample is treated with a freshly prepared solution of ferrous ammonium sulphate followed by potassium thiocyanate solution. The peroxide in the sample oxidizes Fe^{2+} to Fe^{3+} and the latter forms red coloured ferric thiocyanate.

$$Fe^{2+} \xrightarrow{\text{Peroxide}} Fe^{3+} \xrightarrow{SCN^-} \underset{\text{(Red colour)}}{Fe(SCN)_3}$$

To remove peroxide from ether, the sample is washed with ferrous sulphate solution or distilled over concentrated sulphuric acid.

Ring Substitution in Aromatic Ethers

An alkoxy group (—OR) present in an aromatic ether is moderately active and directs the new entering groups to the *ortho*-and *para*-positions. For example:



Anisole o-Nitroanisole p-Nitroanisole

16.17. USES OF ETHERS

Amongst ethers, diethyl ether is the most important. It is used as:

(i) A solvent for oils, fats, gums, resins, etc.
(ii) An extracting solvent for organic substances.
(iii) A refrigerant.
(iv) A general anaesthetic in surgery. Methyl propyl ether also has some anaesthetic use. It is more potent and less irritating to respiratory system than diethyl ether.
(v) An inert medium for organic reactions.

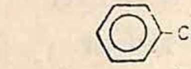
16.18. ALDEHYDES AND KETONES

Aldehydes and ketones are the first oxidation products of primary and secondary alcohols, respectively. They form two isomeric series of carbon compounds having the general formula $R-\underset{\underset{O}{\|}}{C}-H$ for aldehydes and $R-\underset{\underset{O}{\|}}{C}-R'$ for ketones. Here R and R′ could be aliphatic or aromatic and they could be same or different groups. The $\rangle C=O$ group is called *carbonyl group*.

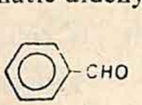
16.19. NOMENCLATURE

Aldehydes

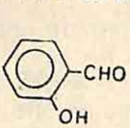
The common (or trivial) names of some aldehydes are given below. The names are derived from the acids obtained from their oxidation. In the IUPAC system, the 'ane' of the corresponding alkane is replaced by 'al'.

Formula	*Common name*	*IUPAC name*
$HCHO$	Formaldehyde	Methanal
CH_3CHO	Acetadehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	*n*-Butyraldehyde	Butanal
$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CHO$	*iso*-Butyraldehyde	2-Methylpropanal
	Phenylacetaldehyde	Phenylethanal

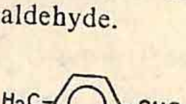
The names of aromatic aldehydes may be derived from the simplest aromatic aldehyde known as benzaldehyde.



Benzaldehyde



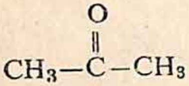
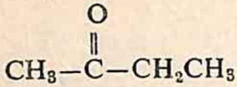
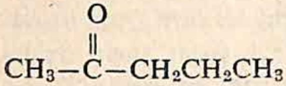
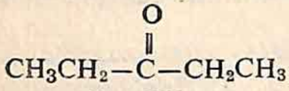
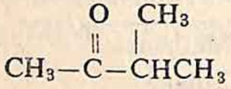
o-Hydroxybenzaldehyde or salicylaldehyde



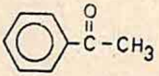
p-Methylbenzaldehyde or tolualdehyde

Ketones

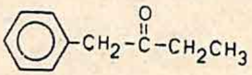
The common name for a ketone is obtained by naming the alkyl groups attached to carbonyl carbon followed by the word ketone. In IUPAC nomenclature, the longest carbon chain including the carbonyl group ($>C=O$) is selected. The carbon chain is numbered from end to end so as to give the lowest number to the carbon of the carbonyl group. The name of the ketone is derived from the corresponding alkane by replacing 'e' of alkane by 'one'.

Formula	*Common name*	*IUPAC name*
 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_3$	Acetone	Propanone
 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2CH_3$	Methyl ethyl ketone	Butanone
 $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2CH_2CH_3$	Methyl *n*-propyl ketone	2-Pentanone
 $CH_3CH_2-\overset{\overset{O}{\parallel}}{C}-CH_2CH_3$	Diethyl ketone	3-Pentanone
 $CH_3-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{CH_3}{\vert}}{C}HCH_3$	Methyl isopropyl ketone	3-Methyl-2-butanone

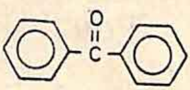
Examples of some aromatic ketones are given below:



Methyl phenyl ketone
or acetophenone



Ethyl Benzyl ketone
or 1-phenyl-2-butanone



Diphenyl ketone or
benzophenone

16.20. STRUCTURE OF CARBONYL GROUP

The carbonyl group ($>C=O$) in aldehydes is connected to one hydrogen and one alkyl or aryl group while in ketones it is attached to two alkyl or aryl groups or one alkyl and one aryl groups. In formaldehyde, the carbonyl group is attached to two hydrogen atoms. This group is responsible for typical reactions of aldehydes and ketones, some of which will be common to both.

In carbonyl group, the carbon and oxygen atoms are linked by a double bond. The carbon atom of $>C=O$ is sp^2 hybridized and is joined to three atoms by σ bonds which including carbon lie in a plane making an angle of 120° with one another (Fig. 16.1). The fourth or p-orbital of carbon atom overlaps with a p-orbital of oxygen atom to form a π bond. Here the π bond connects two atoms of different electronegativities and hence the bonding electrons are not equally shared. Oxygen atom, being more electronegative, pulls the mobile π electrons to itself. This polarization of electrons results in a high dipole moment (2.3 to 2.8 D) for carbonyl compounds.

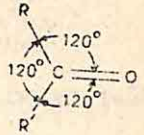
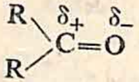


Fig. 16.1 Structure of carbonyl group (R'=H or alkyl).

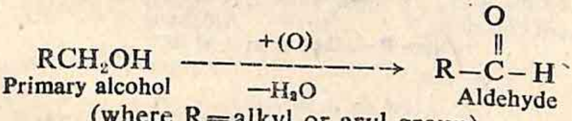


16.21. GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

1. From alcohols

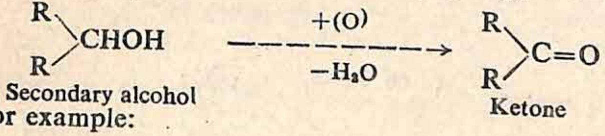
BY DIRECT OXIDATION

Aldehydes are prepared by the oxidation of primary alcohols while ketones by the oxidation of secondary alcohol. Acidified potassium permanganate or potassium dichromate is generally used as the oxidizing agent. Aldehydes are oxidized to carboxylic acids even more readily than alcohols from which they are derived. To control this oxidation, aldehyde formed is immediately distilled out.



$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow[-H_2O]{+(O)} \underset{\text{Aldehyde}}{R-\overset{\displaystyle O}{\overset{\|}{C}}-H}$$

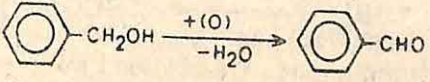
(where R=alkyl or aryl group)



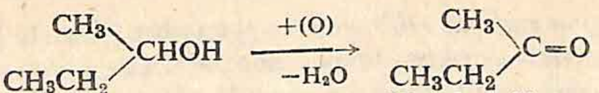
Secondary alcohol Ketone

For example:

$$\underset{n\text{-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[-H_2O]{+(O)} \underset{n\text{-Butyraldehyde}}{CH_3CH_2CH_2CHO}$$



Benzyl alcohol Benzaldehyde



$$\begin{matrix}CH_3\diagdown\\ \quad CHOH\\ CH_3CH_2\diagup\end{matrix} \xrightarrow[-H_2O]{+(O)} \begin{matrix}CH_3\diagdown\\ \quad C=O\\ CH_3CH_2\diagup\end{matrix}$$

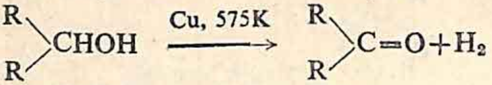
sec-Butyl alcohol — Methyl ethyl ketone

BY CATALYTIC DEHYDROGENATION

When vapours of primary and secondary alcohols are passed over copper gauge at 575K, they are dehydrogenated to aldehydes and ketone respectively.

$$RCH_2OH \xrightarrow{Cu,\ 575K} RCHO+H_2$$

Primary alcohol — Aldehyde



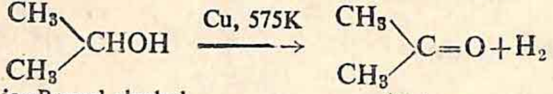
$$\begin{matrix}R\diagdown\\ \quad CHOH\\ R\diagup\end{matrix} \xrightarrow{Cu,\ 575K} \begin{matrix}R\diagdown\\ \quad C=O+H_2\\ R\diagup\end{matrix}$$

Secondary alcohol — Ketone

For example:

$$CH_3CH_2CH_2OH \xrightarrow{Cu,\ 575K} CH_3CH_2CHO+H_2$$

n-Propyl alcohol — Propionaldehyde



$$\begin{matrix}CH_3\diagdown\\ \quad CHOH\\ CH_3\diagup\end{matrix} \xrightarrow{Cu,\ 575K} \begin{matrix}CH_3\diagdown\\ \quad C=O+H_2\\ CH_3\diagup\end{matrix}$$

iso-Propyl alcohol — Acetone

2. From Acid Chlorides

Aldehydes are obtained from acid chlorides by treatment with hydrogen in presence of the catalyst palladium deposited on barium sulphate. This reaction is known as *Rosenmund reduction.*

$$RCOCl+H_2 \xrightarrow{Pd\ on\ BaSO_4} RCHO+HCl$$

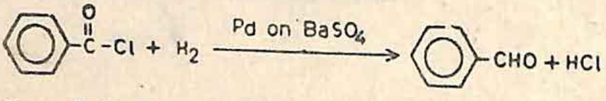
Acid chloride — Aldehyde

(where R=alkyl or aryl group)

For example:

$$CH_3COCl + H_2 \xrightarrow{Pd\ on\ BaSO_4} CH_3CHO + HCl$$

Acetyl chloride — Acetaldehyde



Benzoyl chloride — Benzaldehyde

Ketones are prepared from acid chlorides and organocadmium compounds.

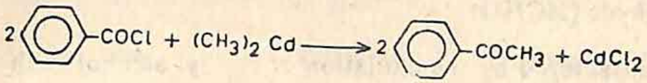
$$2RCOCl + CdR'_2 \longrightarrow 2RCOR' + CdCl_2$$

Acid chloride — Dialkyl cadmium — Ketone

The organocadmium compounds are obtained by reacting Grignard reagent with dry cadmium chloride

$$\underset{\text{Grignard reagent}}{2R'MgX} + CdCl_2 \longrightarrow \underset{\text{Dialkyl cadmium}}{R_2'Cd} + 2MgXCl$$

For example :

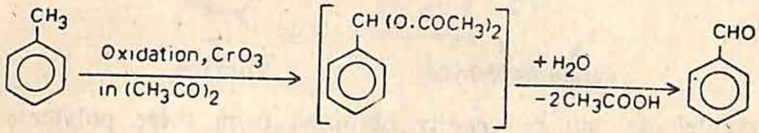


Benzoyl chloride Acetophenone

There are some special methods to prepare aromatic aldehydes and ketones. These are not applicable in the aliphatic series. Some such methods are:

Oxidation of Side-chain Alkyl Groups

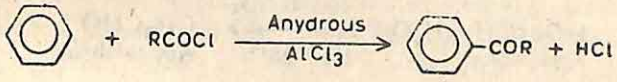
A side chain present in an aromatic compound may be oxidized to —CHO group using chromium trioxide in acetic anhydride.



Toluene Benzaldehyde

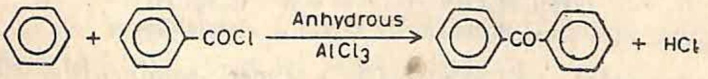
Friedel-Craft Acylation

In this method an aromatic ketone is obtained by treating an aromatic hydrocarbon with an acid chloride in the presence of anhydrous aluminium chloride.



Benzene Acid chloride Ketone

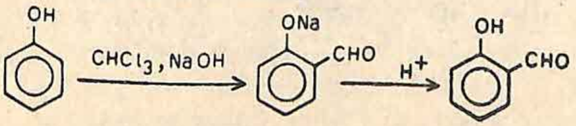
For example:



Benzene Benzoyl chloride Benzophenone

Reimer-Tiemann Reaction

When phenols are heated with chloroform and aqueous alkali, they give phenolic aldehydes. For example:



Phenol Salicylaldehyde

16.22. INDUSTRIAL PREPARATION OF SOME ALDEHYDES AND KETONES

Formaldehyde (HCHO)

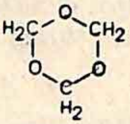
It is manufactured by the oxidation of methyl alcohol with air in the presence of a copper catalyst.

$$\underset{\text{Methyl alcohol}}{CH_3OH} + O_2 \xrightarrow{\text{Cu, 825-875K}} \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

Its 40% aqueous solution is known as *formalin*. It is also available as solid polymers ***paraformaldehyde*** and ***trioxane***.

$$\sim CH_2O-CH_2O-CH_2O \sim$$

Paraformaldehyde



Trioxane

Formaldehyde can be readily obtained from these polymers by gentle warming.

Acetaldehyde (CH_3CHO)

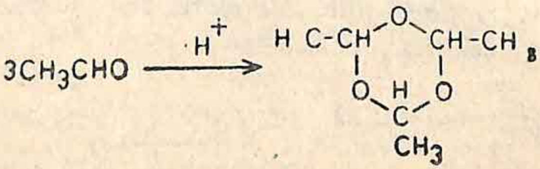
It is manufactured by the hydration of acetylene with dilute sulphuric acid in the presence of mercuric sulphate.

$$\underset{\text{Acetelene}}{HC\equiv CH + H_2O} \xrightarrow[\text{1\% HgSO}_4]{\text{40\% H}_2\text{SO}_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

It may also be obtained by the dehydrogenation of ethyl alcohol,

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[-H_2]{\text{Cu, 575K}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

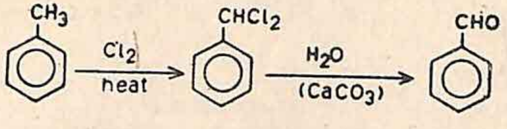
Acetaldehyde is also available as a trimer, ***paraldehyde***, which can be obtained by allowing acetaldehyde to stand for a long time or by adding a drop of concentrated sulphuric acid to it.



Acetaldehyde Paraldehyde

Benzaldehyde (C_6H_5CHO)

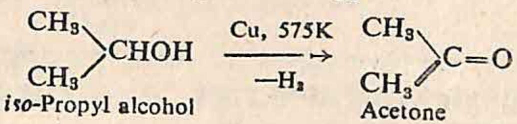
It is manufactured by the side-chain chlorination of toluene followed by alkaline hydrolysis of the product.



Toluene Benzal chloride Benzaldehyde

Acetone (CH_3COCH_3)

The common solvent acetone is manufactured by the dehydrogenation of *iso*-propyl alcohol using heated copper.



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CHOH \xrightarrow[-H_2]{Cu,\ 575K} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C{=}O$$

iso-Propyl alcohol Acetone

During wood distillation, acetone is also obtained as one of the products.

16.23. PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids with a pleasant smell. The higher members are colourless solids. Aromatic ketones are usually solids with a pleasant smell. Some ketones are used in perfumes.

Aldehydes and ketones are polar compounds because of the presence of carbonyl group. As a result they have intermolecular attractions which make them somewhat higher boiling than the hydrocarbons and ethers of comparable molecular masses. These intermolecular attractions are weaker than those due to hydrogen bonds in alcohols and in carboxylic acids. Thus aldehydes and ketones are low boiling liquids than alcohols and acids of comparable masses (Table 16.1).

The lower aldehydes and ketones are soluble in water because of some hydrogen bonding between carbonyl group and water molecules. With increasing molecular size of carbonyl compounds, the influence of the non-polar alkyl group predominates and solubility decreases. They are, of course, soluble in organic solvents.

TABLE 16.1: Polarity and Boiling Point of Molecules with Comparable Molecular Masses

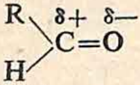
Compound	*Molecular mass*	*Polarity*	*Boiling point, K*
$CH_3CH_2CH_2CH_3$ *n*-Butane	58	Non-polar	273
$CH_3{-}O{-}CH_2CH_3$ Methyl ethyl ether	60	Non-polar	281
CH_3CH_2CHO Propionaldehyde	58	Dipolar	322
CH_3COCH_3 Acetone	58	Dipolar	329
$CH_3CH_2CH_2OH$ *n*-Propyl alcohol	60	Hydrogen bonding	370
CH_3CH_2COOH Propionic acid	60	Hydrogen bonding	391

16.24. CHEMICAL PROPERTIES OF ALDEHYDES AND KETONES

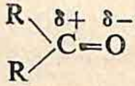
Aldehydes and ketones give the following reactions:

I. Addition Reactions

Due to polarization of $>C=O$ group, the carbon atom gets a partial positive charge and oxygen atom acquires a partial negative charge. This polar nature of carbonyl group gives a number of addition reactions with polar compounds. These addition reactions are also known as *nucleophilic addition reactions*. Aldehydes, however, give addition reactions more readily than ketones.



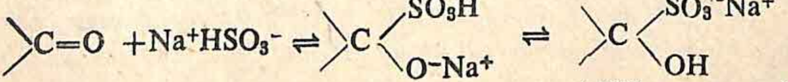
Aldehyde



Ketone

(i) ADDITION OF SODIUM BISULPHITE

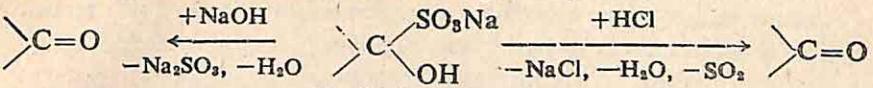
Aldehydes and methyl ketones form crystalline compounds known as *bisulphite compounds* with concentrated solution of sodium bisulphite.



$$>C=O + Na^+HSO_3^- \rightleftharpoons >C\begin{matrix} SO_3H \\ O^-Na^+ \end{matrix} \rightleftharpoons >C\begin{matrix} SO_3^-Na^+ \\ OH \end{matrix}$$

Aldehyde or ketone — Addition compound

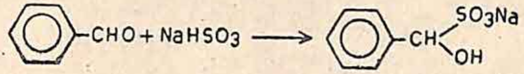
The crystalline compound on treatment with dilute acid or an alkali regenerates the original carbonyl compound.



$$>C{=}O \xleftarrow[-Na_2SO_3,\ -H_2O]{+NaOH} >C\begin{matrix}SO_3Na\\ OH\end{matrix} \xrightarrow[-NaCl,\ -H_2O,\ -SO_2]{+HCl} >C{=}O$$

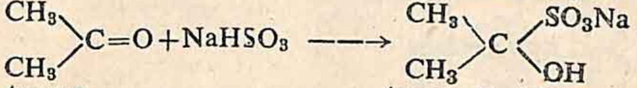
Bisulphite compound

For example:



Benzaldehyde

Benzaldehyde busulphite compound



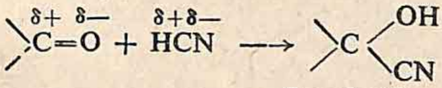
$$\begin{matrix}CH_3\\ CH_3\end{matrix}>C{=}O+NaHSO_3 \longrightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}>C\begin{matrix}SO_3Na\\ OH\end{matrix}$$

Acetone

Acetone bisulphite compound

(ii) ADDITION OF HYDROGEN CYANIDE

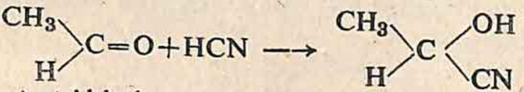
Aldehydes and ketones react with hydrogen cyanide to form cyanohydrins. In actual practice, hydrogen cyanide is generated *in situ* by adding a strong acid to a mixture of sodium cyanide and carbonyl compound. The acid added should be insufficient to consume all the cyanide ions so that the solution remains sufficiently alkaline to act as a catalyst for the reaction.



$$>\overset{\delta+}{C}{=}\overset{\delta-}{O} + \overset{\delta+}{H}\overset{\delta-}{CN} \longrightarrow >C\begin{matrix}OH\\ CN\end{matrix}$$

Cyanohydrin

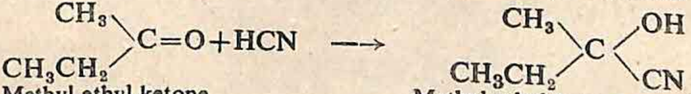
For example:



$$\begin{matrix}CH_3\\ H\end{matrix}>C{=}O+HCN \longrightarrow \begin{matrix}CH_3\\ H\end{matrix}>C\begin{matrix}OH\\ CN\end{matrix}$$

Acetaldehyde

Acetadehyde cyanohydrin

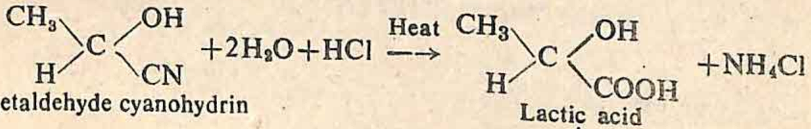


$$\begin{matrix}CH_3\\ CH_3CH_2\end{matrix}>C{=}O+HCN \longrightarrow \begin{matrix}CH_3\\ CH_3CH_2\end{matrix}>C\begin{matrix}OH\\ CN\end{matrix}$$

Methyl ethyl ketone

Methyl ethyl ketone cyanohydrin

Cyanohydrins are used to prepare α-hydroxy acids and unsaturated acids. For example:



$$\begin{matrix}CH_3\\ H\end{matrix}>C\begin{matrix}OH\\ CN\end{matrix} +2H_2O+HCl \xrightarrow{Heat} \begin{matrix}CH_3\\ H\end{matrix}>C\begin{matrix}OH\\ COOH\end{matrix} +NH_4Cl$$

Acetaldehyde cyanohydrin

Lactic acid

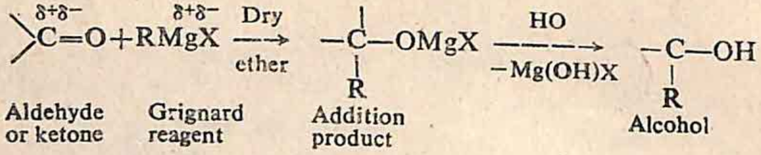
$$\Big\downarrow{\scriptstyle Heat,\ H_2SO_4,\ -H_2O}$$

$$CH_2{=}CHCOOH$$

Acrylic acid

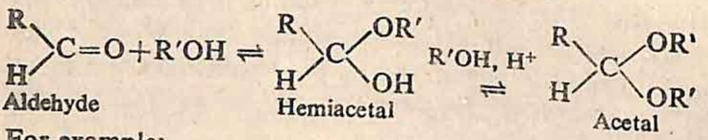
(iii) ADDITION OF GRIGNARD REAGENT

Grignard reagent reacts with an aldehyde or ketone to form an addition product which on hydrolysis yields a primary, a secondary or a tertiary alcohol. This we have already studied under the general methods of preparation of alcohols.

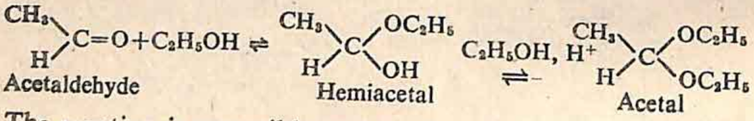


(iv) ADDITION OF ALCOHOL

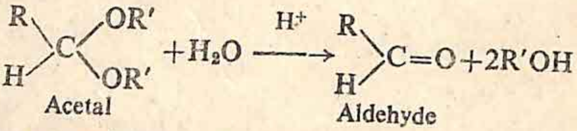
Aldehydes react with alcohols in the presence of dry hydrogen chloride to form *acetals* which contain new bonds between carbonyl carbon and oxygen atoms of the alcohols. The reaction takes place through formation of an unstable *hemiacetal*.



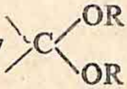
For example:



The reaction is reversible and can be cleaved readily by acids to regenerate aldehydes.



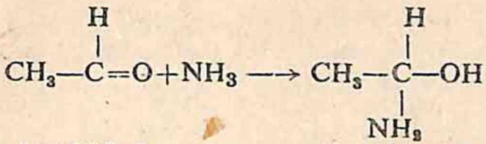
Ketones do not undergo such reactions with alcohols. However, they can indirectly form compounds called *ketals* in which the carbonyl group has been replaced by



group.

(v) ADDITION OF AMMONIA

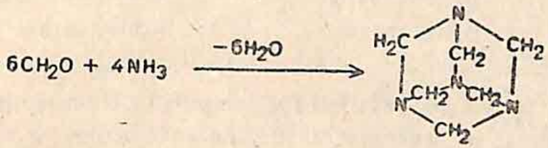
Aldehydes, except formaldehyde and benzaldehyde, react with gaseous ammonia forming addition compounds called *aldehyde ammonia*. For example:



$$CH_3-\overset{H}{\overset{|}{C}}=O+NH_3 \longrightarrow CH_3-\overset{H}{\overset{|}{\underset{\underset{NH_2}{|}}{C}}}-OH$$

Acetaldehyde Acetaldehyde ammonia

Formaldehyde and ammonia react to give hexamethylene tetramine which is used as a urinary antiseptic.



Formaldehyde Hexamethylene tetramine

(vi) ADDITION OF AMMONIA DERIVATIVES

The $\rangle C=O$ group of aldehydes and ketones undergoes reaction with a number of organic compounds containing $-NH_2$ group (ammonia derivatives).

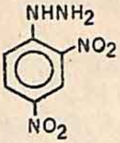
$$\rangle C=O+H_2N-G \xrightarrow{H^+} \rangle C=N-G+H_2O$$

Aldehyde or ketone Ammonia derivative Product

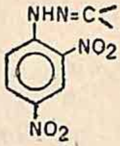
The product produced contains $\rangle C=N-$ group and is usually a crystalline solid with a sharp melting point. It is used for characterization of aldehydes and ketones. Some examples of such ammonia derivatives and the products obtained are given in Table 16.2.

TABLE 16.2: Ammonia Derivatives and Their Products with Carbonyl Compounds

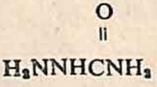
Ammonia derivative	*Product obtained*
NH_2OH Hydroxylamine	$\rangle C=NOH$ Oxime
NH_2NH_2 Hydrazine	$\rangle C=NNH_2$ Hydrazone
$C_6H_5NHNH_2$ Phenyl hydrazine	$\rangle C=NNHC_6H_5$ Phenyl hydrazone



2, 4-Dinitrophenylhydrazine

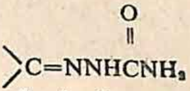


2. 4-Dinitrophenylhydrazone



$$H_2NNH\overset{\overset{O}{\|}}{C}NH_2$$

Semicarbazide



$$>C=NNH\overset{\overset{O}{\|}}{C}NH_2$$

Semicarbazone

The product may also be used for the purification of aldehydes and ketones because it regenerates the parent carbonyl compound on being treated with dilute mineral acid.

Other Reactions

OXIDATION

Aldehydes, because of attachment of hydrogen to carbonyl group, are easily oxidized to acids. Ketones, on the other hand, do not get oxidized easily. Aldehydes are oxidized even by mild oxidizing agents like Tollen's reagent and Fehling's and Benedict's solutions.

Tollen's reagent is ammoniacal silver nitrate. On warming with this reagent, aldehydes form a silver mirror on the walls of the container. Thus:

$$AgNO_3+NH_4OH \longrightarrow AgOH+NH_4NO_3$$

$$AgOH+2NH_3 \longrightarrow [Ag(NH_3)_2]OH$$

$$\underset{\text{Aldehyde}}{RCHO}+2[Ag(NH_3)_2]OH \longrightarrow RCOOH+\underset{\text{(Silver mirror)}}{2Ag}+4NH_3+H_2O$$

Fehling's solution is an alkaline solution of copper sulphate containing sodium potassium tartrate (Rochelle salt) as the complexing agent. Aliphatic aldehydes on warming with this solution, give a red precipitate of cuprous oxide

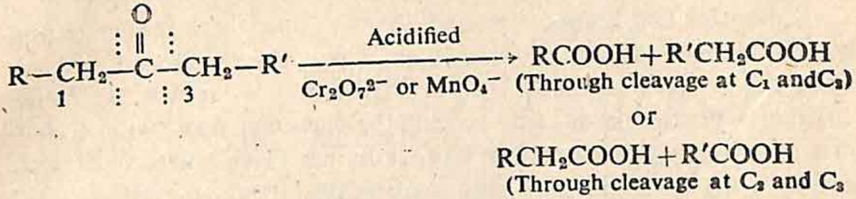
$$CuSO_4+2NaOH \longrightarrow Cu(OH)_2+Na_2SO_4$$

$$Cu(OH)_2 \longrightarrow CuO+H_2O$$

$$RCHO+2CuO \longrightarrow RCOOH+\underset{\text{(Red precipitate)}}{Cu_2O}$$

Aldehydes also reduce the Benedict's solution which is an alkaline solution of copper sulphate containing citrate ions as complexing agent.

Ketones are oxidized with difficulty They do not reduce Tollen's reagent or Fehling's solution. With vigorous oxidizing agent such as acidified dichromate or permanganate, ketones get oxidized with cleavage of carbon-carbon bond giving mixture of acids.



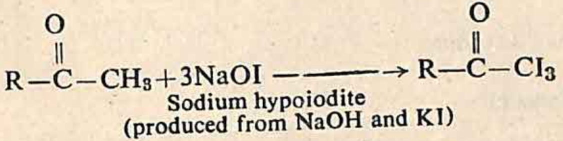
$$\underset{1}{R-CH_2}-\overset{O}{\overset{\|}{C}}-\underset{3}{CH_2}-R' \xrightarrow[Cr_2O_7^{2-} \text{ or } MnO_4^-]{\text{Acidified}} RCOOH+R'CH_2COOH \text{ (Through cleavage at } C_1 \text{ and} C_2)$$

or

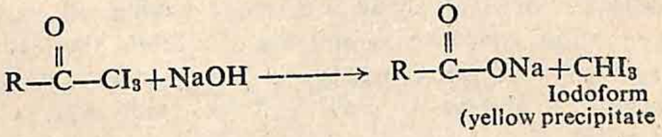
$$RCH_2COOH+R'COOH \text{ (Through cleavage at } C_2 \text{ and } C_3$$

Methyl ketones and acetaldehyde undergo ***haloform reaction*** in which they are reduced easily. The reaction consists in warming the compound with dilute solutions of sodium hydroxide and potassium iodide when a yellow precipitate of iodoform is obtained.

This also serves as a test for the presence of $CH_3-\overset{O}{\overset{\|}{C}}-$ group,



$$R-\overset{O}{\overset{\|}{C}}-CH_3+\underset{\substack{\text{Sodium hypoiodite}\\ \text{(produced from NaOH and KI)}}}{3NaOI} \longrightarrow R-\overset{O}{\overset{\|}{C}}-CI_3$$

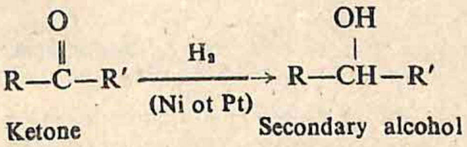


$$R-\overset{O}{\overset{\|}{C}}-CI_3+NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa+\underset{\substack{\text{Iodoform}\\ \text{(yellow precipitate}}}{CHI_3}$$

REDUCTION

Aldehydes and ketones can be reduced to primary and secondary alcohols, respectively. The reduction is done by chemical reducing agents (like lithium aluminium hydride or sodium borohydride) or through catalytic hydrogenation.

$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow[NaBH_4]{LiAlH_4 \text{ or}} \underset{\text{Primary alcohol}}{RCH_2OH}$$



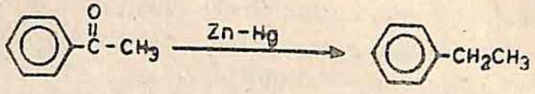
$$\underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R'} \xrightarrow[\text{(Ni ot Pt)}]{H_2} \underset{\text{Secondary alcohol}}{R-\overset{OH}{\overset{|}{C}H}-R'}$$

The catalytic hydrogenation can also reduce the double bond, if present in the molecule. However, sodium borohydride reduces only the carbonyl group. For example:

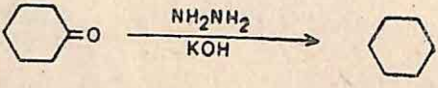
$$H_3C-CH=CH-CH_2OH \xleftarrow{NaBH_4} CH_3CH=CHCHO \xrightarrow[(Ni)]{H_2} CH_3CH_2CH_2CH_2OH$$

Crotyl alcohol Crotonaldehyde *n*-Butyl alcohol

Aldehydes and ketones also undergo *Clemmensen reduction* and *Wolff-Kishner reduction.* Clemmensen reduction is carried out by amalgamated zinc and concentrated hydrochloric acid while Wolff-Kishner reduction is done by heating the carbonyl compound (taken in a high boiling polar solvent like diethylene glycol) with hydrazine and a strong base like potassium hydroxide. For example.



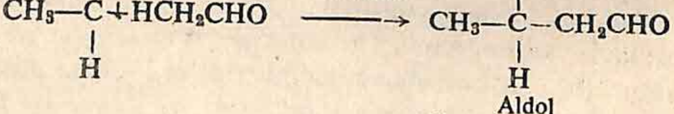
Acetophenone Ethyl benzene



Cyclohexanone Cyclohexane

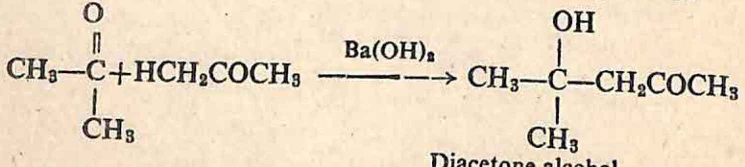
ALDOL CONDENSATION

Two molecules of an aldehyde or a ketone having at least one α-hydrogen atom condense in presence of a dilute alkali to give a β-hydroxyaldehyde or β-hydroxketone. The product obtained from acetadehyde is known as *aldol* and the reaction is called aldol condensation.



$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}+HCH_2CHO \xrightarrow{NaOH} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CHO$$

Aldol
(3-hydroxybutanal)



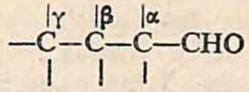
$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{C}}+HCH_2COCH_3 \xrightarrow{Ba(OH)_2} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2COCH_3$$

Diacetone alcohol
(4-hydroxy-4-methyl-2-pentanone)

The condensation product can be easily dehydrated to obtain an α, β-unsaturated carbonyl compound by warming with acid. For example:

$$\underset{\text{Aldol}}{CH_3CH(OH)CH_2CHO} \xrightarrow[\text{warm}]{H^+} \underset{\text{Crotonaldehyde}}{CH_3CH{=}CHCHO}$$

Note. α-Hydrogen is the hydrogen attached to the α-carbon (*i.e.*, the carbon next to the carbon of the carbonyl group),

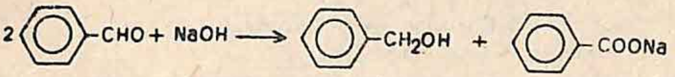


$$-\overset{|\gamma}{\underset{|}{C}}-\overset{|\beta}{\underset{|}{C}}-\overset{|\alpha}{\underset{|}{C}}-CHO$$

CANNIZZARO REACTION

Aldehydes, like formaldehyde or benzaldehyde, which do not have α-hydrogen react with concentrated alkali to give a mixture of alcohol and salt of a carboxylic acid. Thus, one molecule of such an aldehyde is oxidized to acid and the other is reduced to alcohol simultaneously.

$$\underset{\text{Formaldehyde}}{2HCHO} + \underset{\text{(Conc.)}}{NaOH} \longrightarrow \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Sodium formate}}{HCOONa}$$



Benzaldehyde (Conc.) Benzyl alcohol Sodium benzoate

Aldehydes with α-hydrogens form resins when reacted with concentrated alkali.

16.25. TESTS FOR ALDEHYDES AND KETONES

Aldehydes and ketones can be identified through the formation of characteristic crystalline derivatives with reagents like hydroxylamine, 2,4-dinitrophenylhydrazine and semicarbazide. Aldehydes are distinguished from ketones by their reducing capability. They reduce Tollen's reagent, Fehling's solution and Benedict's solution while ketones do not. Methyl ketones and acetaldehyde are characterized through formation of iodoform (haloform reaction).

16.26. CARBOXYLIC ACIDS

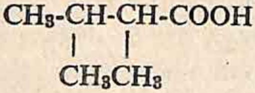
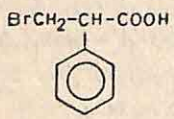
Carboxylic acids have the characteristic $-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ group known as *carboxyl group.* This group may be attached to a saturated or unsaturated alkyl group (—R) or an aryl group (—Ar). Some higher aliphatic carboxylic acids are called fatty acids as they are obtained by the hydrolysis of fats. The carboxylic acids are classified as mono-, di-, tri, ..., or polycarboxylic acids according to the number of carboxyl groups present in them.

16.27. NOMENCLATURE

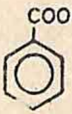
According to the *common system*, the trivial names of carboxylic acids indicate the source from which they are derived. Formic acid was first obtained by the distillation of ants (Latin: *formica* = ant). Acetic acid, butyric acid and caproic acid derive their names from *acetum* (=vinegar), *butyrum* (=butter) and *caper* (goat), respectively. In case of the branch-chain acids, the position of the substituent is indicated by Greek letters α, β, γ, δ, etc. starting from carbon adjacent to carboxylic group.

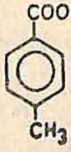
In the *IUPAC system*, the ending 'e' of the corresponding alkane is replaced by 'oic acid'. The longest carbon chain carrying the —COOH group is selected and numbering is done with carboxyl carbon as position one while side chains, if present, get the appropriate numbers.

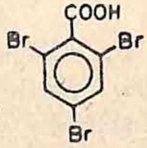
$$-\underset{5\,|}{\overset{\delta\,|}{C}}-\underset{4\,|}{\overset{\gamma\,|}{C}}-\underset{3\,|}{\overset{\beta\,|}{C}}-\underset{2\,|}{\overset{\alpha\,|}{C}}-\underset{1}{COOH}$$

Formula	*Trivial name*	*IUPAC name*
$HCOOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid
 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-\underset{CH_3}{\underset{\vert}{CH}}-COOH$	α,β-Dimethyl butyric acid	2,3-Dimethyl butanoic acid
	β-Bromo-α-phenyl propionic acid	3-Bromo-2-phenyl propionic acid

Names of aromatic acids are usually derived from benzoic acid which is the parent acid.


Benzoic acid


p-Methylbenzoic acid or *p*-toluic acid


2,4,6-Tribromobenzoic acid

16.28. GENERAL METHODS OF PREPARATION OF CARBOXYLIC ACIDS

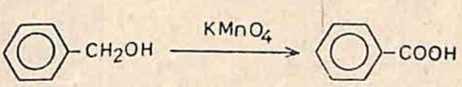
Oxidation Methods

FROM PRIMARY ALCOHOLS

Carboxylic acids are readily obtained by the oxidation of primary alcohols with acidified potassium permanganate or dichromate.

$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow[\text{or } Cr_2O_7^{2-}]{\text{Acidified } MnO_4^-} \underset{\text{Carboxylic acid}}{RCOOH}$$

For Example:



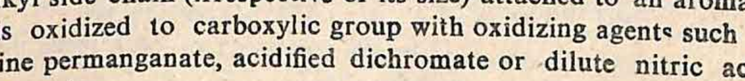
Benzyl alcohol **Benzoic acid**

FROM ALDEHYDES AND KETONES

Even mild oxidizing agent like Tollen's reagent (ammoniacal silver nitrate) can be used for oxidizing aldehydes to carboxylic acids.

$$RCHO \xrightarrow[\text{Tollen's reagent}]{+(O)} RCOOH$$

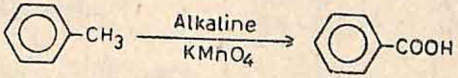
Methyl ketones can also be easily oxidized to carboxylic acids. For example:



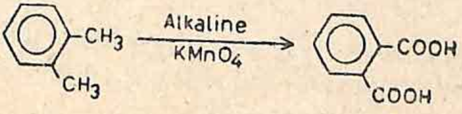
$$\underset{\text{Methyl } n\text{-propyl ketone}}{CH_3CH_2CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3} \xrightarrow{NaOI} \underset{\text{Butyric acid}}{CH_3CH_2CH_2COOH}$$

FROM ALKYL BENZENES

An alkyl side chain (irrespective of its size) attached to an aromatic ring is oxidized to carboxylic group with oxidizing agents such as alkaline permanganate, acidified dichromate or dilute nitric acid. For example:



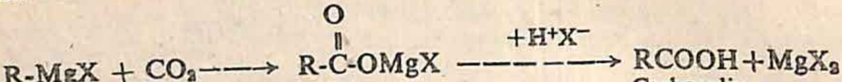
Toluene **Benzoic acid**



o-Xylene **Phthalic acid**

From Grignard Reagent

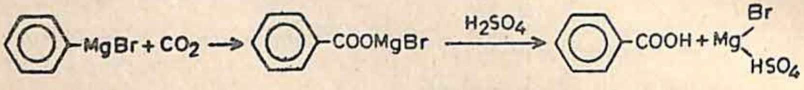
Carboxylic acids are obtained by treating Grignard reagent with carbon dioxide followed by decomposition of the addition product by a mineral acid to liberate the free acid. The reaction is carried out by bubbling gaseous carbon dioxide into the ethereal solution of the Grignard reagent or by pouring the reagent on crushed solid carbon dioxide suspended in ether.



$$\text{R-MgX} + CO_2 \longrightarrow \text{R-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-OMgX} \xrightarrow{+H^+X^-} \text{RCOOH} + MgX_2$$

Grignard reagent — Addition product — Carboxylic acid

For example:



Phenyl magnesium bromide — Addition product — Benzoic acid

From Alkyl Cyanides

When boiled with a dilute alkali or an acid, alkyl cyanides are hydrolysed to carboxylic acids.

$$\underset{\text{Alkyl cyanide}}{\text{R—C}\equiv\text{N} + 2H_2O} \xrightarrow{\text{Alkali}} \underset{\text{Carboxylic acid}}{\text{R-COOH} + NH_3}$$

$$\underset{\text{Alkyl cyanide}}{\text{R—C}\equiv\text{N} + 2H_2O} \xrightarrow{H^+} \underset{\text{Carboxylic acid}}{\text{R-COOH} + NH_4^+}$$

For example:

$$\underset{\text{Ethyl cyanide}}{CH_3CH_2CN} + 2H_2O + HCl \longrightarrow \underset{\text{Propionic acid}}{CH_3CH_2COOH} + NH_4Cl$$

Alkyl cyanides are obtained by the treatment of corresponding alkyl halides with potassium cyanide solution.

$$\underset{\text{Alkyl halide}}{\text{RX} + \text{KCN}} \longrightarrow \underset{\text{Alkyl cyanide}}{\text{RCN} + \text{KX}}$$

16.29. INDUSTRIAL PREPARTION OF SOME CARBOXYLIC ACIDS

Formic Acid (HCOOH). It is generally manufactured by the reaction between carbon monoxide and aqueous sodium hydroxide under a pressure of one atmosphere at 475K.

$$CO + NaOH \xrightarrow[1\ atm]{475K} \underset{\text{Sodium formate}}{HCOONa} \xrightarrow{H^+} \underset{\text{Formic acid}}{HCOOH}$$

Acetic Acid (CH_3COOH.) It is manufactured starting with acetylene or ethyl alcohol. Acetylene is hydrated or ethyl alcohol is dehydrogenated to acetaldehyde. The product is then oxidized to acetic acid with air in the presence of manganous acetate.

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[Mn^{2+}]{+(O)} \underset{\text{Acetic acid}}{CH_3COOH}$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[-H_2]{Cu,\ 575K} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[Mn^{2+}]{+(O)} \underset{\text{Acetic acid}}{CH_3COOH}$$

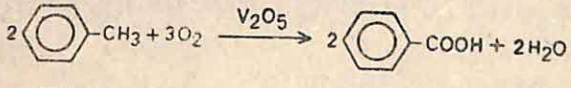
Acetic acid is also obtained in dilute form (called *vinegar*) by the fermentation of ethyl alcohol with bacteria *acetobacter* in the presence of air. This is a very old method for obtaining vinegar.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH + O_2} \xrightarrow{\text{Acetobacter}} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

Higher Carboxylic Acids

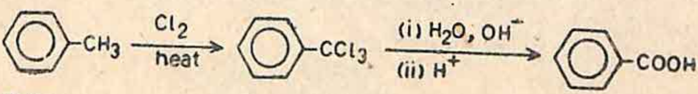
These acids known as *fatty acids* are manufactured by the hydrolysis of naturally occurring oils and fats.

Benzoic Acid (C_6H_5COOH.) It is manufactured by the oxidation of toluene which is readliy available from coal tar or petroleum.



Toluene Benzoic acid

Toluene can also be chlorinated followed by hydrolysis to obtain benzoic acid on a large scale.

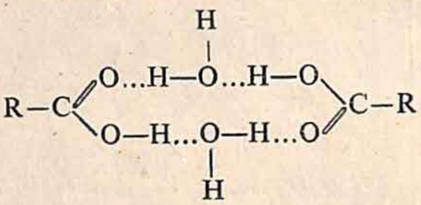


Toluene Benzotrichloride Benzoic acid

16.30. PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

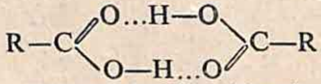
The first three aliphatic acids are colourless mobile liquids with pungent smell. The next six (C_4-C_9) are oily liquids with an odour of rancid butter while the higher members are colourless, odourless waxy solids. Benzoic acid crystallizes in white pearly flakes.

The first four aliphatic members are soluble in water due to intermolecular hydrogen bonding with water molecules.



With increasing size of the alkyl group, the hydrocarbon part of the molecule predominates thereby reducing the water solubility. The higher members are practically insoluble in water.

Carboxylic acids are higher boiling than alcohols of comparable molecular masses (Table 16.1). This is due to the *dimer* formation by intermolecular hydrogen bonding. Molecular-mass determination of the lower carboxylic acids by the vapour-density method gives twice the formula weight because they exist as dimers even in the vapour state.



Hydrogen bonding (dimer)

Benzoic acid sublimes readily and is volatile in steam. Its vapours have an irritating action on nose and throat causing violent coughing and sneezing.

16.31. CHEMICAL PROPERTIES OF CARBOXYLIC ACIDS

Acidity

Next to mineral acids, carboxylic acids are the most acidic amongst the organic compounds. In aqueous solution, they give carboxylate and hydronium ions.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

Applying the law of mass action:

$$K_a = \frac{[RCOO^-]\,[H_3O^+]}{[RCOOH]}$$

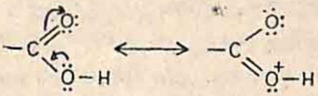
where K_a is known as ***acidity constant*** of the acid. Each acid has its own acidity constant, the larger the value of K_a, the stronger is the acid. Formic acid is stronger than acetic acid while halogen-substituted acids are even much stronger acids than formic acid (Table 16.3).

TABLE 16.3: Acidity Constants of some Carboxylic Acids

Name	*Formula*	$K_a \times 10^5$
Formic acid	$HCOOH$	17.7
Acetic acid	CH_3COOH	1.75
Propionic acid	CH_3CH_2COOH	1.3
Chloroacetic acid	$ClCH_2COOH$	136
Dichloroacetic acid	$Cl_2CHCOOH$	5530
Trichloroacetic acid	Cl_3CCOOH	23200
Fluoroacetic acid	FCH_2COOH	260
Bromoacetic acid	$BrCH_2COOH$	125
Iodoacetic acid	ICH_2COOH	67

CAUSE OF ACIDITY

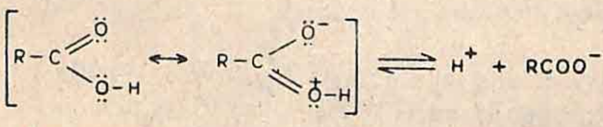
The carboxyl group is a resonance hybrid of the following two structures:



(I) (II)

These structures are non-equivalent, differ considerably in energy and do not make equal contribution to the resonance hybrid. Therefore the resonance energy is quite low.

In the resonance hybrid, oxygen of the hydroxyl group carries some positive charge. The electron pair of the O—H bond is thus displaced towards oxygen and the hydrogen of the O—H bond is released as H^+ ion along with the formation of a carboxylate ion. Thus:

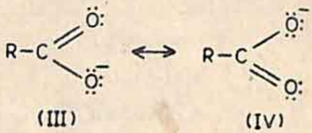


Less stabilized, non-equivalent structures of carboxylic acid

Carboxylate ion

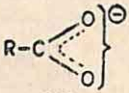
It explains the acidic nature of the carboxyl group.

Now, let us see the structure of carboxylate ion. This is also a resonance hybrid in which the structures (III) and (IV) make equal contribution because they are alike. Thus, the resonance energy of carboxylate ion is much higher than that of the acid itself. This leads to greater stabilization of carboxylate ion. Carboxylic acids will, therefore, dissociate to more stabilized carboxylate ions and release H^+ ions.



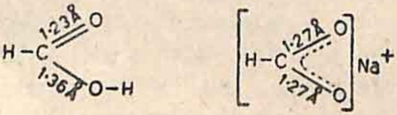
More stabilized equivalent structures of carboxylate ion.

The similar structures (III) and (IV) may be represented as:



(V)

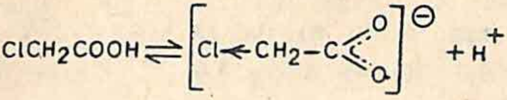
This shows that the negative charge is evenly distributed over the two oxygen atoms and the carbon is attached to each oxygen by *one and a half* bond. This is supported by the measurement of bond lengths in formic acid and sodium formate. In formic acid, carbon oxygen bond lengths are different (1.23Å for double bond and 1.36Å for single bond) while they have the same value (1.27Å) in case of sodium formate.



EFFECT OF SUBSTITUENTS ON ACIDITY

We know that if the same charge (positive or negative) on an ion is increased, it becomes less stable. The carboxylate ion, which carries a negative charge, will be destabilized if the negative charge on it is increased or intensified. On the other hand, it will be stabilized if the negative charge is decreased or dispersed from it.

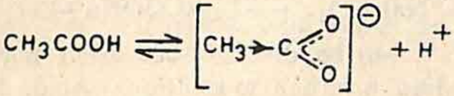
In acetic acid, the methyl group being electron-donating, will intesify the negative charge on carboxylate ion and destabilize it.



Acetic acid

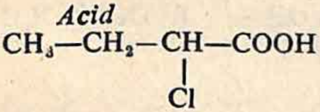
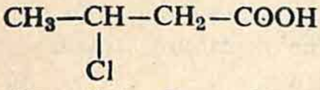
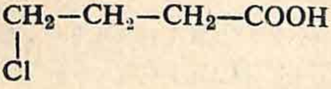
The equilibrium will be shifted more towards left-hand side and not favour ionization. This explains why acetic acid is weaker than formic acid which has hydrogen attached to carboxylate ion (Table 16.3).

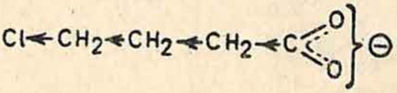
In chloroacetic acid, the electron-withdrawing effect of chlorine stabilizes the anion due to dispersal of negative charge favouring a high degree of ionization. Chloroacetic acid is 100 times stronger than acetic acid (Table 16.3). Further, the strength is increased by increasing the number of halogen atoms. Thus dichloroacetic acid is a stronger acid than monochloroacetic acid and trichloroacetic acid is still stronger (Table 16.3).



Chloroacetic acid

The electron-withdrawing effect of halogen decreases very rapidly with distance from the carboxyl group. Thus with increasing distance between halogen and carboxyl group, the acidity decreases as it is evident from the following data:

Acid	$K_a \times 10^5$
 $CH_3-CH_2-\underset{\underset{Cl}{\vert}}{CH}-COOH$	139
 $CH_3-\underset{\underset{Cl}{\vert}}{CH}-CH_2-COOH$	8.9
 $\underset{\underset{Cl}{\vert}}{CH_2}-CH_2-CH_2-COOH$	2.96



Electron-withdrawing effect of halogen decreases with distance from the carboxyl group.

Also, stronger the electron-withdrawing group, greater is the acidity of the acid. Thus, fluoroacetic acid is stronger than chloroacetic acid and the latter is stronger than bromo and iodoacetic acids (Table 16.3). Benzoic acid is stronger ($K_a = 6.5 \times 10^{-5}$) than simple aliphatic acids because phenyl group is more electron-withdrawing than alkyl group.

(i) **Action of metals.** Metals like sodium, potassium, zinc and magnesium react with carboxylic acids evolving hydrogen. For example:

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Mg \longrightarrow \underset{\text{Magnesium acetate}}{(CH_3COO)_2Mg} + H_2$$

(ii) **Action of alkalis.** Carboxylic acids react with alkalis to form salts.

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

Carboxylic acids can be distinguished from phenols by their reactions with sodium bicarbonate solution. Acids dissolve evolving carbon dioxide while most phenols do not react with bicarbonate solution.

Conversion to Acid Derivatives

ESTERS (RCOOR′)

These are obtained by treating acids with alcohols in the presence of concentrated sulphuric acid or dry hydrogen chloride.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH} \xrightarrow{H^+} \underset{\text{Ester}}{RCOOR'} + H_2O$$

ACID CHLORIDES (RCOCL)

These are obtained when the acids are treated with phosphorus pentachloride or thionyl chloride.

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{Acid chloride}}{RCOCl} + SO_2 + HCl$$

ACID AMIDES ($RCONH_2$)

These are obtained from acids by treating them with ammonia followed by heating the ammonium salt formed.

$$\underset{\text{Acid}}{RCOOH} + NH_3 \longrightarrow \underset{\text{Ammoium salt}}{RCOONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acid amide}}{RCONH_2} + H_2O$$

ACID ANHYDRIDES [$(RCO)_2O$]

An acid anhydride is obtained by treating a carboxylic acid with the corresponding acid chloride in the presence of pyridine.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Acid chloride}}{RCOCl} \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Acid anhydride}}{(RCO)_2O}$$

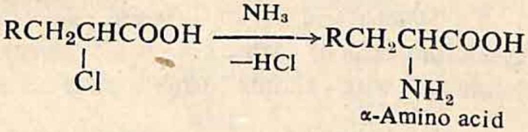
α-Halogenation of Aliphatic Acids

In the presence of a small amount of phosphorus, the α-hydrogens of carboxylic acids can be replaced by chlorine and bromine atoms. Thus chlorine attacks acetic acid replacing all hydrogen atoms successively.

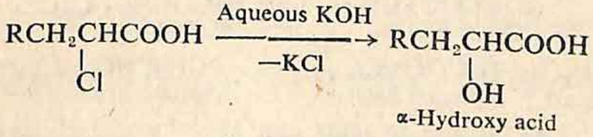
$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[P]{Cl_2} \underset{\text{Chloroacetic acid}}{CH_2ClCOOH} \xrightarrow[P]{Cl_2} \underset{\text{Dichloroacetic acid}}{CHCl_2COOH} \xrightarrow[P]{Cl_2} \underset{\text{Trichloroacetic acid}}{CCl_3COOH}$$

This reaction is known as *Hell-Volhard-Zelinsky (HVR) reaction.*

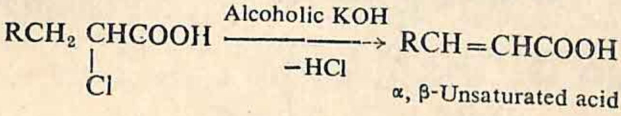
The reaction has a great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products. For example:



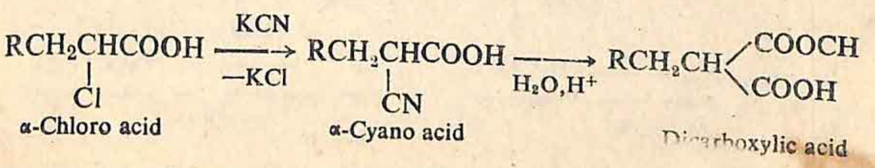
$$RCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH \xrightarrow[-HCl]{NH_3} \underset{\text{α-Amino acid}}{RCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH}$$



$$RCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH \xrightarrow[-KCl]{\text{Aqueous KOH}} \underset{\text{α-Hydroxy acid}}{RCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCOOH}$$



$$RCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH \xrightarrow[-HCl]{\text{Alcoholic KOH}} \underset{\text{α, β-Unsaturated acid}}{RCH{=}CHCOOH}$$



$$\underset{\text{α-Chloro acid}}{RCH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCOOH} \xrightarrow[-KCl]{KCN} \underset{\text{α-Cyano acid}}{RCH_2\underset{\displaystyle CN}{\underset{|}{C}}HCOOH} \xrightarrow[H_2O,H^+]{} \underset{\text{Dicarboxylic acid}}{RCH_2CH\begin{matrix}\diagup COOCH\\ \diagdown COOH\end{matrix}}$$

Reduction

Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride.

$$\underset{\text{Acid}}{RCOOH} \xrightarrow{LiAlH_4} \underset{\text{Primary alcohol}}{RCH_2OH}$$

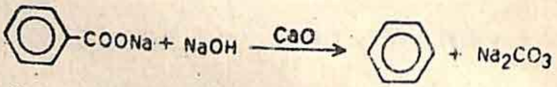
Decarboxylation

When sodium salts of some carbxylic acids are heated with sodalime (a mixture of NaOH and CaO), they are decarboxylated to hydrocarbons.

$$\underset{\text{(Sodium salt)}}{RCOONa} + NaOH \xrightarrow{CaO} \underset{\text{Hydrocarbon}}{RH} + Na_2CO_3$$

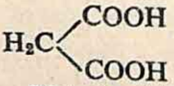
For example:

$$\underset{\text{Sodium acetate}}{CH_3COONa} + NaOH \xrightarrow{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$



Sodium benzoate Benzene

Dicarboxylic acids having two carboxyl groups attached to the same carbon atom are readily decarboxylated simply on heating.



$$\underset{\text{Malonic acid}}{H_2C(COOH)_2} \xrightarrow{415\text{-}435K} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

Heating calcium salts of carboxylic acids gives ketones, while heating calcium salt with calcium formate gives an aldehyde.

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Acetone}}{CH_3COCH_3} + CaCO_3$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium formate}}{(HCOO)_2Ca} \longrightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2CaCO_3$$

Alkali salts of carboxylic acids can also be decarboxylated on electrolysis.

$$2RCOONa \rightleftharpoons 2RCOO^- + 2Na^+$$

$$-2e^- \downarrow \qquad \downarrow +2e^-$$

$$\underbrace{R-R+CO_2 \longleftarrow 2RCOO}_{\text{At anode}} \qquad \underbrace{2Na \xrightarrow{+2H_2O} 2NaOH + H_2}_{\text{At cathode}}$$

For example:

$$2CH_3COONa \rightleftharpoons 2CH_3COO^- + 2Na^+$$

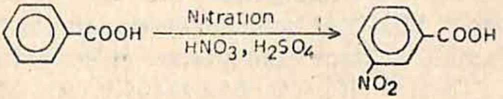
$$-2e^- \downarrow \qquad\qquad \downarrow +2e^-$$

$$\underbrace{\underset{\text{Ethane}}{C_2H_6}+2CO_2 \leftarrow 2CH_3COO}_{\text{At anode}} \qquad \underbrace{2Na \xrightarrow{+2H_2O} 2NaOH+H_2}_{\text{At cathode}}$$

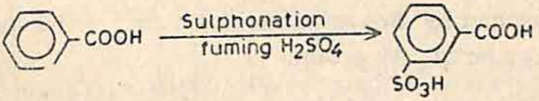
Kolbe used this electrolytic method to obtain alkanes from carboxylic acids. It is known as *Kolbe electrolytic reaction.*

Ring Substitution in Aromatic Acids

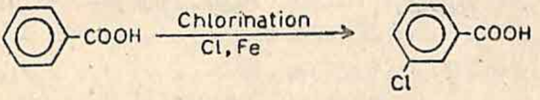
Aromatic carboxylic acids undergo usual substitution reactions of benzene ring. Carboxyl group being an electron withdrawing group, it is *meta*-directing.



Benzoic acid m-Nitrobenzoic acid



Benzoic acid m-Sulphobenzoic acid



Benzoic acid m-Chlorobenzoic acid

16.32. FUNCTIONAL DERIVATIVES OF ACIDS

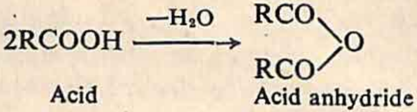
These are the derivatives of carboxylic acids in which —OH part of carboxyl group is replaced by some other group. They are known as acid chlorides, acid anhydrides, acid amides and esters.

Acid Chlorides (RCOCl)

These are derived from carboxylic acides by replacement of the —OH part of —COOH group by a chlorine atom. In naming them by the common system or the IUPAC system, the terminal 'ic acid' is changed into 'yl chloride'. Some examples are given in Table 16.4.

Acid Anhydrides [$(RCO_2)O$]

When two —OH groups of two monocarboxylic acids lose one molecule of water, an acid anhydride is obtained.



$$2RCOOH \xrightarrow{-H_2O} \begin{matrix} RCO \searrow \\ \quad O \\ RCO \nearrow \end{matrix}$$

Acid Acid anhydride

In both the systems of naming the compounds, the suffix 'acid' is changed into 'anhydride' (Table 16.4).

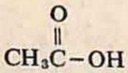
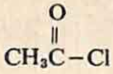
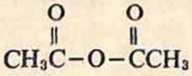
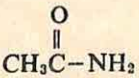
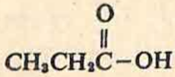
Acid Amides ($RCONH'_2$)

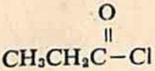
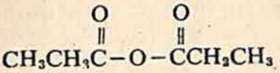
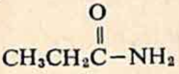
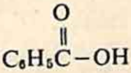
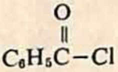
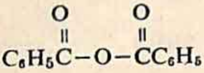
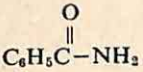
These are derived from acids by replacing —OH of the —COOH group with $—NH_2$. In naming them, the suffix 'ic acid' of common name or 'oic acid' of IUPAC name of corresponding acid is changed to the suffix 'amide', Some examples are given in Table 16.4.

Esters (RCOOR')

An ester is formed by the replacement of the —OH part of carboxyl group by an alkoxy group.

TABLE 16.4 : Common and IUPAC Names of Functional Derivatives of Acids

	Formula	*Common name*	*IUPAC name*
Acid	 $CH_3\overset{O}{\overset{\|}{C}}-OH$	Acetic acid	Ethanoic acid
Acid chloride	 $CH_3\overset{O}{\overset{\|}{C}}-Cl$	Acet*yl* *chloride*	Ethano*yl* *chloride*
Acid anhydride	 $CH_3\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}CH_3$	Acetic *anhydride*	Ethanoic *anhydride*
Acid amide	 $CH_3\overset{O}{\overset{\|}{C}}-NH_2$	Acet*amide*	Ethan*amide*
Acid	 $CH_3CH_2\overset{O}{\overset{\|}{C}}-OH$	Propionic acid	Propanoic acid

Acid chloride	 $CH_3CH_2\overset{\overset{O}{\|}}{C}-Cl$	Propion*yl chloride*	Propiono*yl chloride*
Acid anhydride	 $CH_3CH_2\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}CH_2CH_3$	Propionic *anhydride*	Propanoic *anhydride*
Acid amide	 $CH_3CH_2\overset{\overset{O}{\|}}{C}-NH_2$	Propion*amide*	Propan*amide*
Acid	 $C_6H_5\overset{\overset{O}{\|}}{C}-OH$	Benzoic acid	Benzoic acid
Acid chloride	 $C_6H_5\overset{\overset{O}{\|}}{C}-Cl$	Benzo*yl chloride*	Benzo*yl chloride*
Acid anhydride	 $C_6H_5\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}C_6H_5$	Benzoic *anhydride*	Benzoic *anhydride*
Acid amide	 $C_6H_5\overset{\overset{O}{\|}}{C}-NH_2$	Benz*amide*	Benz*amide*

16.33. METHODS OF PREPARATION OF FUNCTIONAL DERIVATIVES OF ACIDS

Acid Chlorides

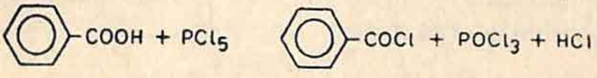
These are obtained from carboxylic acids by treatment with phosphorus pentachloride, phosphorus trichloride or thionyl chloride.

$$RCOOH+PCl_5 \longrightarrow RCOCl+POCl_3+HCl$$
$$RCOOH+PCl_3 \longrightarrow RCOCl+H_3PO_3$$
$$RCOOH+SOCl_2 \longrightarrow RCOCl+HCl+SO_2$$

(where R=alkyl or aryl group)

For example:

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{Acetyl chloride}}{CH_3COCl}+SO_2+HCl$$

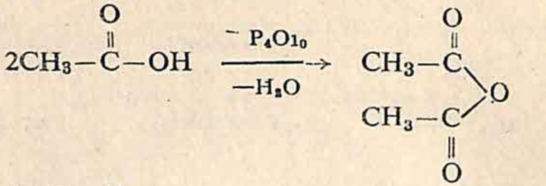


Benzoic acid Benzoyl chloride

The use of thionyl chloride is preferred as both the by-products SO_2 and HCl, are gaseous and it is easier to obtain the acid chloride in a pure form.

Acid Anhydrides

These are obtained by the dehydration of acids with a strong dehydrating agent like phosphorus pentoxide. For example:



Acetic acid Acetic anhydride

Acid anhydrides may also be obtained by treating acid chlorides with carboxylic acid in the presence of a base like pyridine. For example:

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-HCl]{\text{Pyridine}} \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

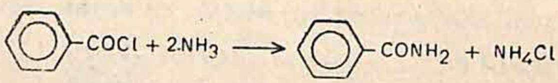
Acid Amides

These can be readily obtained by the action of ammonia on the other acid derivatives. For example:

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + 2HN_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + NH_4Cl$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + 2NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + CH_3CONH_4$$

$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + CH_3OH$$



Benzoyl chloride Benzamide

Nitriles, on treatment with alkaline hydrogen peroxide, undergo partial hydrolysis and give acid amides.

$$\underset{\text{Acetonitrile}}{CH_3CN} + 2H_2O_2 \xrightarrow{OH^-} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O + O_2$$

Ammonium salts of carboxylic acids are thermally decomposed to obtain acid amides on large scale. For example:

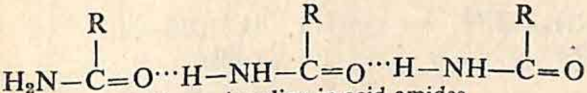
$$\underset{\text{Ammonium salt}}{RCOO^-NH_4^+} \xrightarrow{\text{Heat}} \underset{\text{Acid amide}}{RCONH_2} + H_2O$$

For Example:

$$\underset{\text{Ammonium acetate}}{CH_3COO^-NH_4^+} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

16.34. PHYSICAL PROPERTIES OF ACID DERIVATIVES

These are polar compounds. Hydrogen bonding is not possible in acid chlorides and acid anhydrides so they remain as unassociated molecules. Amides form intermolecular hydrogen bonding and are generally solids (except formamide which is a liquid) at room temperature. Their boiling points are higher compared to those of the corresponding acids or other derivatives. Acid chlorides boil at lower temperature than the corresponding acids but anhydrides possess higher boiling points due to their molecular masses being double (Table 16.5).



$$H_2N-\overset{\overset{R}{|}}{C}=O\cdots H-NH-\overset{\overset{R}{|}}{C}=O\cdots H-NH-\overset{\overset{R}{|}}{C}=O$$

Hydrogen bonding in acid amides

TABLE 16.5: Melting and Boiling Points of some Acids and Their Functional Derivatives

Compound	*Melting point, K*	*Boiling point, K*
Acetic acid	289.6	391.0
Acetyl chloride	161	324
Acetic anhydride	200	413
Acetamide	355	494
Benzoic acid	395	522
Benzoyl chloride	272	470
Benzoic anhydride	315	633
Benzamide	403	563

Acid derivatives are soluble in common organic solvents. Acid chlorides and anhydrides are decomposed by water. Amides are more soluble in water than the other derivatives due to hydrogen bonding with water.

Acid chlorides and anhydrides have sharp irritating smell and cause watering from eyes and nose.

16.35. CHEMICAL PROPERTIES OF ACID DERIVATIVES

Acid derivatives undergo substitution reactions in which the functional group is replaced by some other group.

(i) Hydrolysis

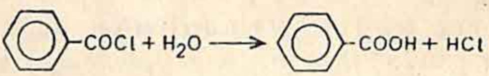
By hydrolysis (with water or preferably in acidic or alkaline medium), the derivatives give back the parent acids.

$$\underset{\text{Acid chloride}}{RCOCl+H_2O} \longrightarrow \underset{\text{Acid}}{RCOOH+HCl}$$

$$\underset{\text{Acid anhydride}}{(RCO)_2O+H_2O} \longrightarrow \underset{\text{Acid}}{2RCOOH}$$

$$\underset{\text{Acid amide}}{RCONH_2+H_2O} \longrightarrow \underset{\text{Acid}}{RCOOH+NH_3}$$

For example:



Benzoyl chloride Benzoic acid

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O+H_2O} \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH}$$

$$\underset{\text{Propionamide}}{CH_3CH_2CONH_2+H_2O} \longrightarrow \underset{\text{Propionic acid}}{CH_3CH_2COOH+NH_3}$$

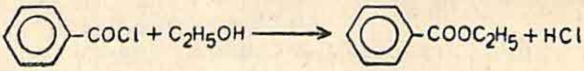
(ii) Alcoholysis

Acid chlorides and acid anhydrides react with alcohols to form esters.

$$\underset{\text{Acid chloride}\quad\text{Alcohol}}{RCOCl+R'OH} \longrightarrow \underset{\text{Ester}}{RCOOR'+HCl}$$

$$\underset{\text{Acid anhydride}}{(RCO)_2O+R'OH} \longrightarrow \underset{\text{Ester}}{RCOOR'+RCOOH}$$

For example:



Benzoyl chloride Ethyl benzoate

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O+C_2H_5OH} \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}+CH_3COOH$$

(iii) Ammonolysis

As it has been discussed under the preparation of amides, the acid derivatives react with ammonia to form amides. For example:

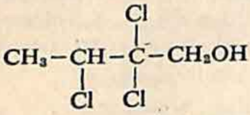
$$\underset{\text{Acetyl chloride}}{CH_3COCl+2NH_3} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}+NH_4Cl$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O+2NH_3} \dashrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}+CH_3COONH_4$$

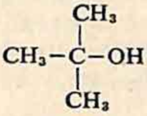
$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5+NH_3} \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2}+C_2H_5OH$$

EXERCISES

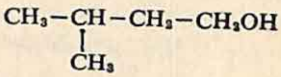
16.1 What are alcohols? How are they classified? Write the IUPAC names for the following alcohols :



$CH_3-\underset{\underset{Cl}{|}}{CH}-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2OH$



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2OH$

16.2 How are alcohols obtained from aldehydes and ketones?

16.3 What are the industrial methods of obtaining alcohols? Give their uses.

16.4 How is phenol obtained industrially? What are its uses?

16.5 Why have alcohols and phenols higher boiling points compared to the corresponding hydrocarbons ? Give generals physical characteristics of alcohols and phenol.

16.6 Discuss the reactions of alcohols involving the cleavage of
 (i) Oxygen-hydrogen bond.
 (ii) Carbon-oxygen bond.

16.7 What happens when phenol is (i) Halogenated, (ii) Nitrated and (iii) Sulphonated? What are Kolbe's and Riemer-Tiemann reactions?

16.8 How will you distinguish various types of alcohols? Give some characteristic tests of phenols.

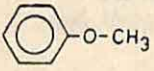
16.9 What do you understand by the following terms:

(i) Absolute alcohol	(ii) Industrial alcohol
(iii) Power alcohol	(iv) Denatured alcohol

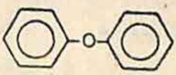
16.10 What are symmetrical and unsymmetrical ethers? Give the common and IUPAC names for the following ethers:

$C_2H_5OC_2H_5$

(i)



(ii)



(iii)

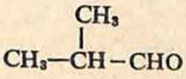
16.11 What is Williamson synthesis? Give the physical characteristics of ethers.

16.12 What happens when an ether undergoes cleavage? Give important uses of ethers?

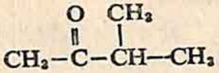
16.13 What are aldehydes and ketones? Give the common and IUPAC names for the following compounds:

(i) $CH_3CH_2CH_2CHO$

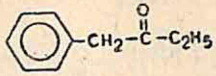
(ii)



$CH_3-\overset{\overset{CH_3}{|}}{CH}-CHO$

(iii) 

$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

(iv) 

(iv)

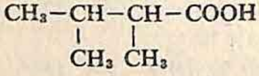
16.14 Write notes on the following:
- (i) Structure of carbonyl group
- (ii) Rosemund reaction
- (iii) Friedel-Craft acylation
- (iv) Trioxane

16.15 What are the general methods of obtaining aldehydes and ketones? How are they tested?

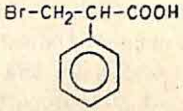
16.16 Discuss the reactions of aldehydes and ketones under the following heads:
- (i) Addition reactions
- (ii) Oxidation
- (iii) Reduction

16.17 What is aldol condensation? What happens when aldol is dehydrated?

16.18 What are carboxylic acids? How are they named? Give the trivial and IUPAC names for the following:



$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-COOH$



16.19 How are carboxylic acids obtained from:
- (i) Primary alcohols
- (ii) Aldehydes
- (iii) Alkyl cyanides
- (iv) Grignard reagents

16.20 How is benzoic acid manufactured? Discuss its physical properties.

16.21 Explain the cause of acidity in carboxylic acids.

16.22 How will you obtain the following from carboxylic acids:
- (i) Acid chlorides
- (ii) Acid amides
- (iii) Acid anhydrides

16.23 What is HVR reaction? Explain its synthetic importance.

16.24 Give suitable examples of functional derivatives of acids. Give their common as well as IUPAC names.

16.25 Explain why the acid chlorides boil at lower temperature than the corresponding acids but the acid anhydrides possess higher boiling points.

16.26 Discuss the chemical properties of acid chlorides, acid anhydrides and acid amides under the following heads.
- (i) Hydrolysis
- (ii) Alcoholysis
- (iii) Ammonolysis

Unit 17

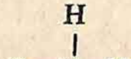
Compounds with Functional Groups Containing Nitrogen

Amines and Nitro Compounds: Nomenclature; Ethylamine, aniline.

In this Unit, we shall study two main classes of organic compounds in which nitrogen forms a part of the functional group. These are: Amines and Nitro compounds.

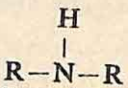
17.1. AMINES

Amines may be regarded as alkyl- or aryl-substituted derivatives of ammonia. They are classified as primary, secondary or tertiary amines according to the number of alkyl or aryl groups attached to nitrogen. Thus:



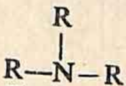
$R-\overset{H}{\overset{|}{N}}-H$

Primary amine



$R-\overset{H}{\overset{|}{N}}-R$

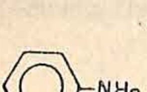
Secondary amine



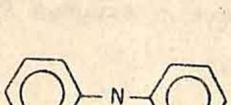
$R-\overset{R}{\overset{|}{N}}-R$

Tertiary amine

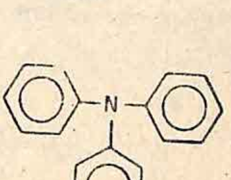
When one or more aryl groups are substituted into ammonia, the amine is called an aromatic amine. For example:



Aniline



Diphenylamine



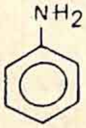
Triphenylamine

17.2. NOMENCLATURE

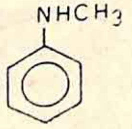
Amines are commonly named by writing the names of alkyl or aryl groups followed by the suffix amine. In IUPAC system of nomenclature, the word amino (or N-alkylamino in case of secondary and N,N-dialkylamino in case of tertiary amines) is prefixed before the name of the parent compound consisting of the longest possible straight chain. The positions of various groups are numbered according to the general IUPAC rules. Both common and IUPAC names of some amines are given below:

Amine	*Common name*	*IUPAC name*
CH_3NH_2	Methylamine	Aminomethane
$CH_3CH_2NH_2$	Ethylamine	Aminoethane
$CH_3CH_2CH_2NH_2$	*n*-Propylamine	1-Aminopropane
$CH_3\underset{\underset{CH_3}{\vert}}{C}HNH_2$	*iso*-Propylamine	2-Aminopropane
CH_3NHCH_3	Dimethylamine	N-Methylaminomethane
$CH_3\underset{\underset{CH_3}{\vert}}{N}CH_3$	Trimethylamine	N, N-Dimethylaminomethane

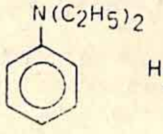
Aromatic amines are generally named as derivatives of the simplest aromatic amine, aniline. Thus:



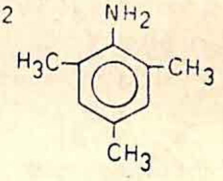
Aniline



N-Methylaniline

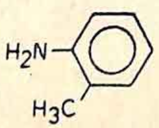


N, N-Diethylaniline

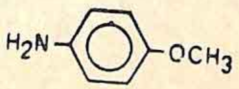


2,4,6-Trimethylaniline

Sometimes, the arylamines are also assigned special names. For example:



o-Toluidine



p-Anisidine

17.3. LABORATORY PREPARATION

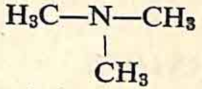
Amines may be prepared in the laboratory by the following methods:

From Alkyl Halides (Ammonolysis)

By heating an alkyl halide such as methyl iodide with alcoholic ammonia in a sealed tube, a mixture of all the three classes of amines is obtained together with quaternary compound.

$$CH_3I + NH_3 \xrightarrow[-HI]{373K} \underset{\text{Methylamine (primary)}}{CH_3NH_2}$$

$$CH_3NH_2 + CH_3I \xrightarrow{-HI} \underset{\text{Dimethylamine (secondary)}}{CH_3NHCH_3}$$



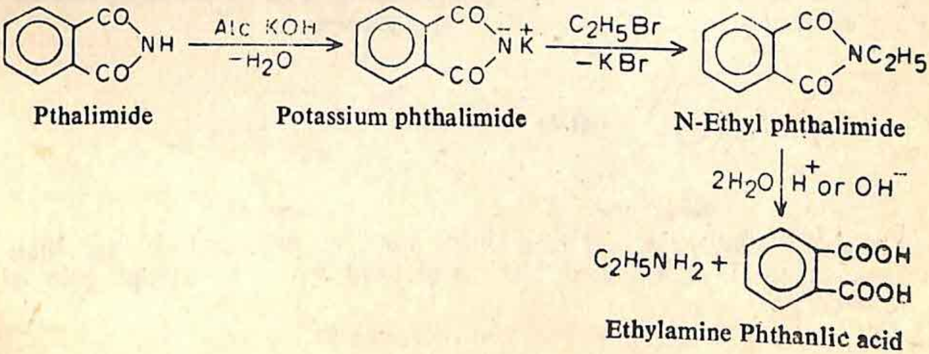
$$CH_3NHCH_3 + CH_3I \xrightarrow{-HI} \underset{\text{Trimethylamine (tertiary)}}{H_3C{-}\underset{\overset{|}{CH_3}}{N}{-}CH_3}$$

$$(CH_3)_3N + CH_3I \xrightarrow{-HI} \underset{\text{Quaternary ammonium iodide}}{[(CH_3)_4N]^+I^-}$$

The composition of the mixture obtained varies with the ratio of the reactants taken. However, the primary amine predominates if large excess of ammonia is used. Because it is difficult to separate the mixture, the method is not of much practical importance.

From Phthalimide (Gabriel's Synthesis)

This method is used for primary amines. Phthalimide is treated with alcoholic KOH to give potassium phthalimide which gives N-alkyl phthalimide with alkyl halide. The product on hydrolysis with 20% HCl under pressure or refluxing with KOH gives primary amine.

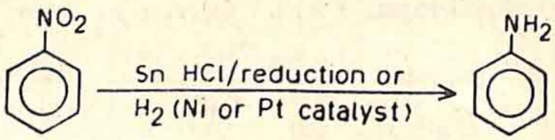


Pthalimide Potassium phthalimide N-Ethyl phthalimide

Ethylamine Phthanlic acid

From Nitro Compounds

Nitro compounds on reduction yield primary amines. This method is particularly useful for aromatic amines. The reduction is carried out by using hydrochloric acid and a cheap metal like tin, iron or zinc. Catalytic reduction with hydrogen in presence of nickel or platinum can also be performed.



Aliphatic nitro compounds can also be reduced to corresponding amines by lithium aluminium hydride.

From Cyanides

Cyanides on catalytic hydrogenation or reduction with sodium and alcohol (*Mendius reaction*) give primary amines.

$$\underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{+4H} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

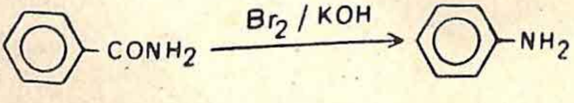
Secondary amines are obtained by similar reduction of isocyanides.

$$\underset{\text{Methyl isocyanide}}{CH_3NC} \xrightarrow{+4H} \underset{\text{Dimethylamine}}{CH_3NHCH_3}$$

From Acid Amides (Hofmann Bromamide Reaction)

This consists in treating an amide with bromine and alkali to yield an amine. For example:

$$\underset{\text{Acetamide}}{CH_3CONH_2}+Br_2+4KOH \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2}+2KBr+K_2CO_3+2H_2O$$



Benzamide Aniline

In this method, the resulting amine contains one carbon less than the original amide and thus the method is used for stepping down the series.

17.4. INDUSTRIAL PREPARATION

The industrial methods of preparation of some simpler amines are given below:

Aliphatic Amines: Such as methylamine, dimethylamine and trimethylamine are manufactured by passing vapours of methyl alcohol and ammonia over heated alumina (at 723 K).

$$\underset{\text{Methanol}}{CH_3OH} \xrightarrow[-H_2O]{NH_3} \underset{\text{Methylamine}}{CH_3NH_2} \xrightarrow[-H_2O]{CH_3OH} \underset{\text{Dimethylamine}}{(CH_3)_2NH} \xrightarrow[-H_2O]{CH_3OH} \underset{\text{Trimethylamine}}{(CH_3)_3N}$$

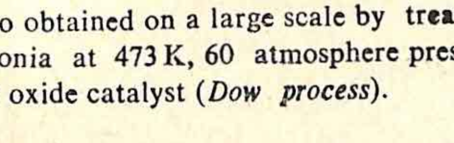
The mixture of different amines can be separated by fractional distillation.

Ethanol and ammonia may be used to manufacture corresponding ethylamines.

The most important aromatic amine, *aniline* is manufactured by the reduction of nitrobenzene with iron and steam in the presence of hydrochloric acid. The acid helps to release hydrogen from steam. As the acid is regenerated, only a small quantity is required in the process.

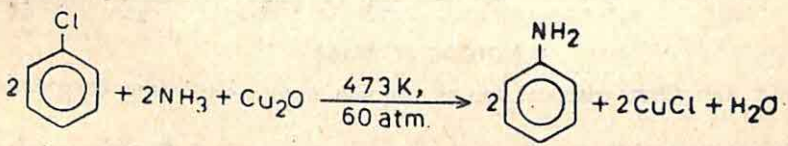
$$Fe + 2HCl \longrightarrow FeCl_2 + 2H$$

$$FeCl_2 + \underset{\text{Steam}}{2H_2O} \longrightarrow Fe(OH)_2 + \underset{\text{(Regenerated)}}{2HCl}$$



Nitrobenzene Aniline

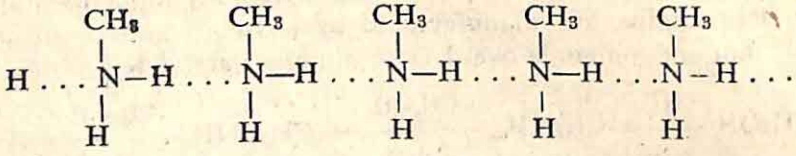
Aniline is also obtained on a large scale by treating chlorobenzene with ammonia at 473 K, 60 atmosphere pressure and in presence of cuprous oxide catalyst (*Dow process*).



17.5. PHYSICAL PROPERTIES

The lower members of aliphatic amines are gases with smell of ammonia while higher members are mostly liquids with fishy odour. Aromatic amines are either liquids with unpleasant odours or low melting solids.

Like ammonia, amines are polar compounds and, except for tertiary amines, can form intermolecular hydrogen bonds.



$$\mathrm{H}\ldots\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{N}\\ |\\ \mathrm{H}\end{array}\!\!-\mathrm{H}\ldots\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{N}\\ |\\ \mathrm{H}\end{array}\!\!-\mathrm{H}\ldots\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{N}\\ |\\ \mathrm{H}\end{array}\!\!-\mathrm{H}\ldots\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{N}\\ |\\ \mathrm{H}\end{array}\!\!-\mathrm{H}\ldots\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{N}\\ |\\ \mathrm{H}\end{array}\!\!-\mathrm{H}\ldots$$

Due to hydrogen bonding, they have higher boiling points than non-polar compounds of nearly the same molecular masses but lower than corresponding alcohols or carboxylic acids (Fig. 17.1). This is because the electronegativity of nitrogen is lower than that of oxyen and hence hydrogen bonding in amines is weaker compared to that in alcohols or carboxylic acids.

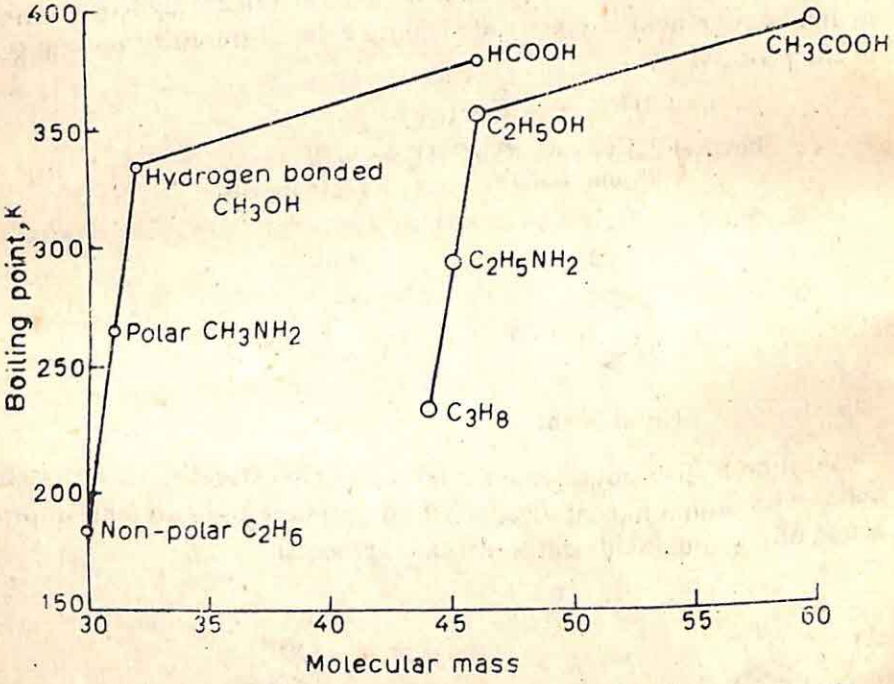
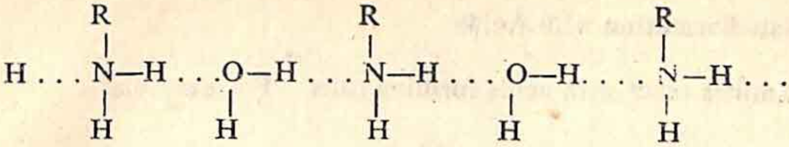


Fig. 17.1 Comparison of boiling points of amines with other compounds.

Amines of all the three classes are capable of forming hydrogen bonds with water. As a result, lower amines are quite soluble in water, with borderline solubility being reached at about six carbon atoms.



$$H\cdots\underset{H}{\overset{R}{N}}-H\cdots\underset{H}{O}-H\cdots\underset{H}{\overset{R}{N}}-H\cdots\underset{H}{O}-H\cdots\underset{H}{\overset{R}{N}}-H\cdots$$

Amines are soluble in less polar solvents like benzene, ether, alcohol, etc. Aromatic amines are insoluble in water but soluble in benzene, ether and alcohol.

Aromatic amines are very toxic and are very easily oxidized by air and get coloured on keeping, though they are colourless when freshly prepared and pure.

17.6. CHEMICAL PROPERTIES

Basic Nature

Like ammonia, all aliphatic amines are basic in nature due to an unshared pair of electrons on the nitrogen atom. In fact, they are more basic than ammonia due to the presence of alkyl groups which increase the availability of electrons on the nitrogen atom. In case of aryl amines, the basic character is less as the aryl group attracts electrons from the nitrogen atom. Like ammonia, they dissolve in water to form quaternary ammonium hydroxides. The dissociation constant, K_b is an index of the basic power of an amine. Each amine has its own dissociation constant. The larger the value of K_b, the stronger will be the base.

$$RNH_2+H_2O \longrightarrow RNH_3OH \rightleftharpoons RNH_3^+ + OH^-$$

$$K_b=\frac{[RNH_3^+][OH^-]}{[RNH_3OH]}$$

K_b values for ammonia and some amines are given in Table 17·1.

TABLE 17.1 : K_b Values of Ammonia and Some Amines

Base	K_b	*Base*	K_b
NH_3	1.8×10^{-5}	$C_2H_5NH_2$	4.7×10^{-4}
CH_3NH_2	4.4×10^{-4}	$(C_2H_5)_2NH$	9.5×10^{-4}
$(CH_3)_2NH$	5.1×10^{-4}	$(C_2H_5)_3N$	5.5×10^{-4}
$(CH_3)_3N$	0.6×10^{-4}	$C_6H_5NH(CH_3)$	7.1×10^{-10}
$C_6H_5NH_2$	4.2×10^{-10}	$C_6H_5N(CH_3)_2$	11.0×10^{-10}

Salt Formation with Acids

Amines react with acids forming salts. For example:

$$C_2H_5NH_2 + HCl \longrightarrow C_2H_5\overset{+}{N}H_3Cl^-$$

Ethylamine — Ethyl ammonium chloride

$$2CH_5NH_2 + H_2PtCl_6 \longrightarrow (C_6H_5\overset{+}{N}H_3)_2PtCl_6^{2-}$$

Aniline — Choloro-platinic acid — Aniline chloroplatinate

Salts of amines with picric acid are used for the identification of amines. Chloroplatinates (salts of amines with chloroplantinic acid) are used for determination of equivalent and molecular masses of amines.

Reaction with Nitrous Acid

Different amines react differently with nitrous acid (produced *in situ* by the action of a mineral acid such as hydrochloric acid on sodium nitrite). . The reactions are carried out at low temperatures (273-278K).

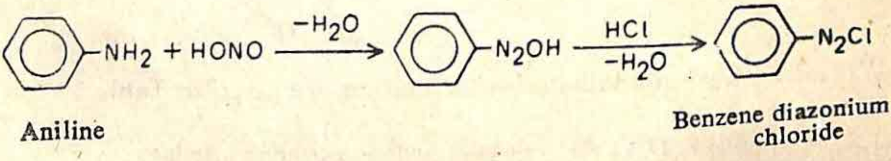
WITH PRIMARY AMINES

Primary aliphatic amines react to give alcohols. For example:

$$CH_3NH_2 + HONO \xrightarrow{-H_2O} CH_3N_2OH \longrightarrow CH_3OH + N_2$$

Methylamine — (Unstable diazonium compound) — Methanol

Aromatic amines form diazonium salts. For example:



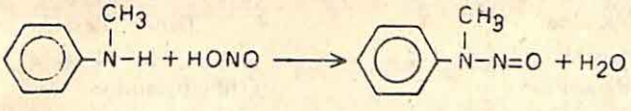
Aniline — Benzene diazonium chloride

WITH SECONDARY AMINES

Both aliphatic and aromatic amines form nitrosoamines slowly, *nitrogen is not evolved*. The compounds, unlike parent amines, are yellow coloured, neutral and insoluble in dilute mineral acids.

$$(CH_3)_2NH + HONO \longrightarrow (CH_3)_2N{-}N{=}O + H_2O$$

Dimethylamine — Dimethyl-N-nitrosoamine



N-Methylaniline Methylphenyl-N-nitrosoamine

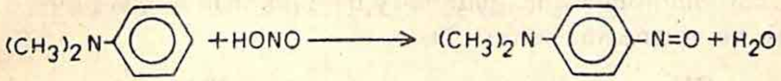
WITH TERTIARY AMINES

Aliphatic amines form addition salts called trialkyl ammonium nitrites. For example:

$$(CH_3)_3N + HONO \longrightarrow [(CH_3)_3NH]^+NO_2^-$$

Trimethylamine Trimethyl ammonium nitrite

Aromatic amines undergo ring substitution, generally at *para* position, to give water soluble *para* nitroso compounds. The introduction of $-N=O$ group in the benzene ring is called *nitrosation*.

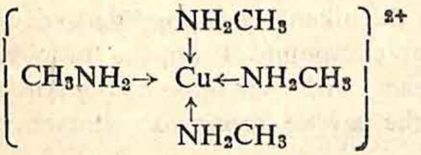


Dimethylaniline *p*-Nitroso-N, N-dimethylaniline

Thus, reaction with nitrous acid can be used to distinguish primary, secondary and tertiary amines.

Reaction with Metal Ions

Similar to the reactions of ammonia, amines also form complexes with metal ions. For example, silver chloride dissolves in methylamine to give, $[Ag(CH_3NH_2)_2]^+Cl^-$. Cupric salt solution forms a deep blue complex with methylamine corresponding to the structure:



$$\left[\begin{array}{c} NH_2CH_3 \\ \downarrow \\ CH_3NH_2 \rightarrow Cu \leftarrow NH_2CH_3 \\ \uparrow \\ NH_2CH_3 \end{array}\right]^{2+}$$

Reaction with Alkyl Halides or Alkylation

Like ammonia, amines react with alkyl halides to form the next higher class of amines. Thus, a primary amine can be converted into a secondary amine, a secondary into a tertiary and finally a tertiary amine into a quaternary ammonium salt. Thus:

$$\underset{\text{Methylamine}}{CH_3NH_2} + CH_3I \longrightarrow \underset{\text{Dimethylamine}}{(CH_3)_2NH} + HI$$

$$\underset{\text{Dimethylamine}}{(CH_3)_2NH} + CH_3I \longrightarrow \underset{\text{Trimethylamine}}{(CH_3)_3N} + HI$$

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + CH_3I \longrightarrow \underset{\text{Quaternary ammonium iodide}}{(CH_3)_4NI}$$

This reaction of amines with methyl iodide leading to the formation of quaternary ammonium salt is called *exhaustive methylation.*

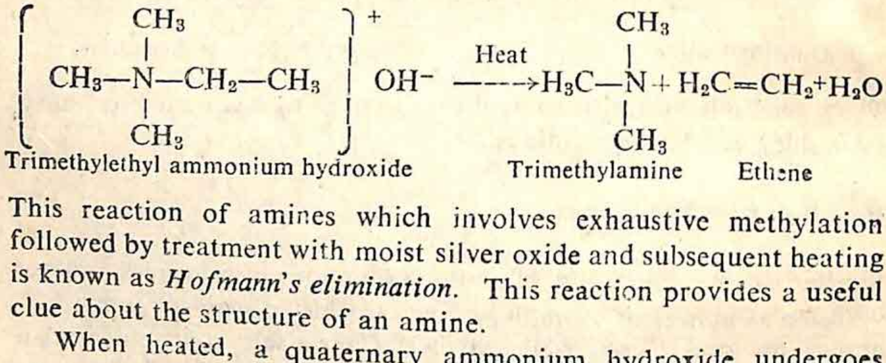
On treatment with moist silver oxide, the quaternary salts give quaternary ammonium hydroxide (a base).

$$(CH_3)_4NI \xrightarrow{\text{Moist } Ag_2O} (CH_3)_4\overset{+}{N}OH^-$$

The base is ionic in nature and is as basic as NaOH or KOH. It decomposes on heating as shown:

$$(CH_3)_4NOH \xrightarrow{389K} \underset{\text{Trimethylamine}}{(CH_3)_3N} + \underset{\text{Methanol}}{CH_3OH}$$

If one of the alkyl groups is other than methyl (i.e., it has two or more carbon atoms), the quaternary base on heating gives a tertiary amine, an alkene and water. Thus:



$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3-N-CH_2-CH_3 \\ | \\ CH_3 \end{array}\right]^+ OH^- \xrightarrow{\text{Heat}} \begin{array}{c} CH_3 \\ | \\ H_3C-N \\ | \\ CH_3 \end{array} + H_2C{=}CH_2 + H_2O$$

Trimethylethyl ammonium hydroxide Trimethylamine Ethene

This reaction of amines which involves exhaustive methylation followed by treatment with moist silver oxide and subsequent heating is known as *Hofmann's elimination.* This reaction provides a useful clue about the structure of an amine.

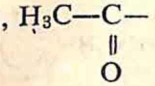
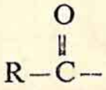
When heated, a quaternary ammonium hydroxide undergoes elimination to an alkene and a tertiary amine. From the structures of these two, especially the alkene, it is possible to deduce the structure of the parent amino compound. From the number of moles of methyl iodide that react with one mole of the amine, it can also be deduced whether the amino group is primary, secondary or tertiary.

$$RCH_2CH_2NH_2 + 3CH_3I \xrightarrow{-2HI} [RCH_2CH_2N(CH_3)_3]^+I^-$$

$$\Big\downarrow \text{AgOH}$$

$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + \underset{\text{Alkene}}{RCH{=}CH_2} + H_2O \xleftarrow{\text{Heat}} \underset{\text{Quaternary ammonium hydroxide}}{[RCH_2CH_2N(CH_3)_3]^+OH^-}$$

Reaction with Acid Chlorides or Acid Anhydrides, Acylation

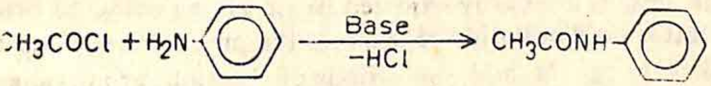
Primary and secondary amines react with acetyl chloride or acetic anhydride to give acetyl derivatives. The reaction introduces acetyl group,  $H_3C-\underset{\underset{O}{\|}}{C}-$, in the molecule and is known as *acetylation*. In general, the introduction of  $R-\overset{\overset{O}{\|}}{C}-$ group in the compound is called *acylation*.

$$C_2H_5NH_2+CH_3COCl \xrightarrow[-HCl]{Base} C_2H_5NHCOCH_3$$

Ethylamine N-Ethylacetamide

The reaction is carried out in the presence of some base such as pyridine or sodium hydroxide to neutralize HCl formed. The acylation with acid anhydrides is slower.

Aniline reacts with acetyl chloride to give acetanilide.

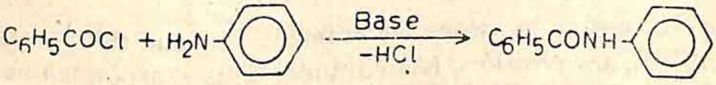


Acetyl chloride Acetanilide

Tertiary amines do not have hydrogen attached nitrogen and hence they are not acetylated.

Benzoylation

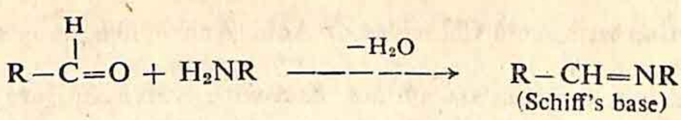
It is the introduction of benzoyl group, $C_6H_5CO^-$, into the compound by benzoyl chloride in presence of a base. *Benzoylation* of aniline gives benzanilide.



Benzoyl chloride Benzanilide

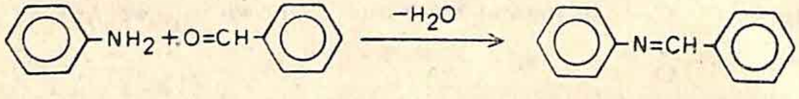
Reaction with Aldehydes

Aliphatic primary amines and aniline react with aldehydes to give Schiff's bases.



$$\mathrm{R{-}\overset{\displaystyle H}{\overset{|}{C}}{=}O + H_2NR \xrightarrow{-H_2O} R{-}CH{=}NR}$$

(Schiff's base)

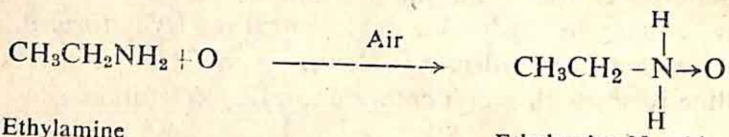


Aniline Benzaldehyde Benzalanilide

Schiff's bases on reduction give secondary amines. The method may be used for their preparation.

Oxidation

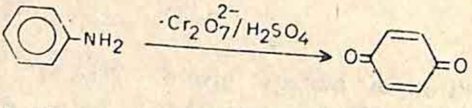
Aliphatic amines on oxidation in air give N-oxides. For example:



$$\mathrm{CH_3CH_2NH_2 + O \xrightarrow{Air} CH_3CH_2{-}\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{N}}}{\rightarrow}O}$$

Ethylamine Ethylamine-N-oxide

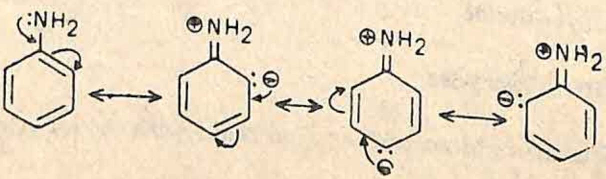
Aromatic amines are easily oxidized in air giving coloured products but the latter on distillation regenerate the pure amines. Depending on oxidizing agents and conditions of reaction, aromatic amines give different products. For example, on oxidation with dichromate and sulphuric acid, aniline gives a black dye called *aniline black*. With the same oxidizing agent but under controlled conditions, aniline is oxidized to *p*-benzoquinone.



Aniline p-Bezoquinone

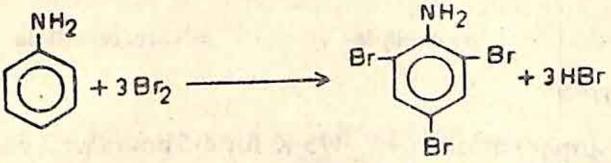
Ring Substitution in Aromatic Amines

The amino group activates the aromatic ring and the substitution at *ortho* and *para* positions is facilitated. This is explained as under by delocalization of electrons:



HALOGENATION

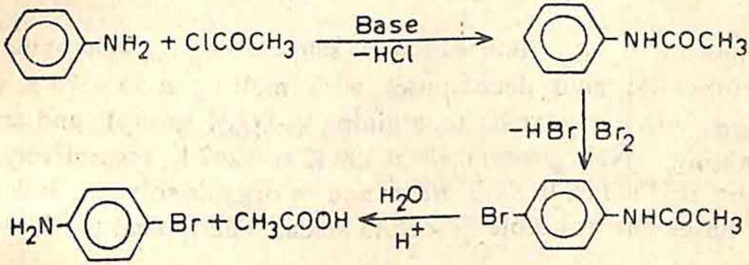
Aqueous bromine activates the amino group in aniline to such an extent that bromine enters the *para* as well as both the *ortho* positions in the molecule giving 2,4,6-tribromoaniline.



Aniline

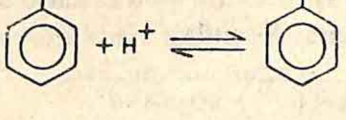
2, 4, 6-Tribromoaniline

To get a monobromo compound, the amino group is acetylated before bromination. After bromination, the anilide is acid-hydrolyzed to yield the desired halogenated amine. Thus:



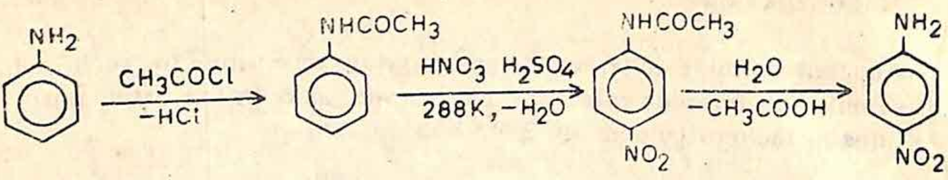
NITRATION

Nitric acid, besides being a nitrating agent, is also a strong oxidizing agent. Therefore, aniline when treated with nitric acid, forms tarry oxidation products. Moreover, in a strongly acidic medium, the amino group takes up a proton to form anilinium ion:



Nitrogen in the anilinium ion no longer possesses an unshared pair of electrons but has a positive charge and directs a large percentage of the entering groups to the *meta* position.

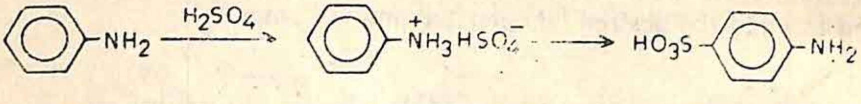
Thus, to carry out nitration, aniline is first acetylated and then nitrated. This intermediate step of acetylation protects the amino group and is known as *protecting the amino group*. The acetyl group is subsequently removed by hydrolysis.



Aniline Acetanilide *p*-Nitroacetanilide *p*-Nitroaniline

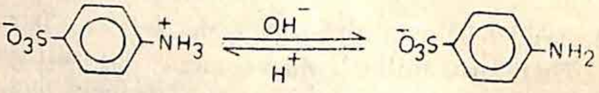
SULPHONATION

Aniline on sulphonation at 455-475 K for 4-5 hours with concentrated sulphuric acid gives *p*-aminobenzene sulphonic acid (commonly called ***sulphanilic acid***). The process of sulphonation of aniline is called *baking*.



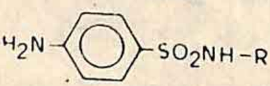
Aniline Aniline hydrogen sulphate Sulphanilic acid

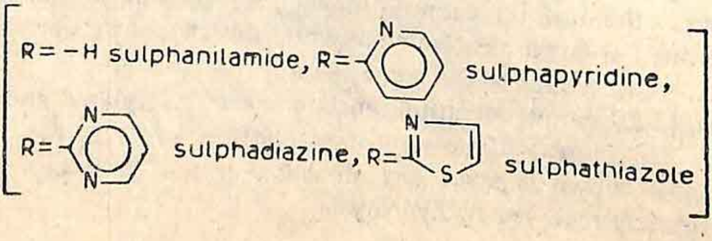
Sulphanilic acid decomposes with melting at 553-573 K while benzene sulphonic acid (containing $-SO_3H$ group) and aniline (containing $-NH_2$ group) melt at 339 K and 267 K, respectively. Sulphanilic acid is insoluble in water and in organic solvents. It is soluble in bases but insoluble in dilute acids. The typical behaviour of sulphanilic acid is because it contains both $-\overset{+}{N}H_3$ and $-SO_3^-$ *ionic* groups in the same molecule. Thus it is a *dipolar or zwitter ion.*



(Water-insoluble) (Water soluble)

The amides of sulphonic acid are known as ***sulphonamides*** or ***sulpha drugs***. Many of them are used as antibiotics. They may be represented by the general formula:





17.7. DETECTION OF AMINES

Amines are soluble in dilute hydrochloric acid due to their basicity.

The three classes of amines can be distinguished by reaction with benzene sulphonyl chloride (*Hinsberg's reagent*) in the presence of sodium hydroxide or potassium hydroxide. A primary amine reacts to give a clear solution which on acidification yields an insoluble material.

$$\underset{\text{Hinsberg's reagent}}{RNH_2 + C_6H_5SO_2Cl} \xrightarrow{OH^-} \underset{\substack{\text{N-substituted}\\ \text{sulphonamide}}}{C_6H_5SO_2NHR} \xrightarrow{KOH} \underset{\substack{\text{Potassium salt of}\\ \text{sulphonamide,}\\ \textit{clear solution}}}{C_6H_5SO_2NR^-K^+}$$

$$\downarrow H^+$$

$$\underset{\substack{\text{Sulphonamide regenerated,}\\ \textit{insoluble}}}{C_6H_5SO_2NHR}$$

A secondary amine forms an insoluble compound which does not react with an acid.

$$R_2NH + C_6H_5SO_2Cl \xrightarrow{OH^-} \underset{\substack{\text{N,N-Disubstituted}\\ \text{sulphonamide, }\textit{insoluble}}}{C_6H_5SO_2NR_2} \xrightarrow{H^+} \text{No reaction}$$

A tertiary amine remains unreacted with the reagent but dissolves in acid.

$$\underset{\text{(Unreacted)}}{R_3N + H^+} \longrightarrow \underset{\text{(Clear solution)}}{[R_3NH]^+}$$

Primary amines (aliphatic or aromatic) when heated with chloroform and an alkali give a characteristic offensive smell of isocyanide. The test is called *isocyanide test.* Secondary and tertiary amines do not respond to this test.

$$\underset{\text{Primary amine}}{RNH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\substack{\text{Isocyanide}\\ \text{(offensive smell)}}}{R{-}N\overset{\rightarrow}{=}C} + 3KCl + 3H_2O$$

Primary amines require three moles of an alkyl halide to give quaternary compounds, secondary amines require two and tertiary one mole.

$$RNH_2 \xrightarrow[-HI]{RI} R_2NH \xrightarrow[-HI]{RI} R_3N \xrightarrow[-HI]{RI} R_4NI$$

17.8. USES OF AMINES

Amines are put to a veriety of uses. For example, aromatic amines are used as intermediates in the manufacture of drugs, textiles and photographic developers. Through formation of diazonium salts, $ArN_2^+X^-$ (where Ar=aromatic ring and X^-= anion like Cl^-, Br^-, etc.), they form a large number of intensely coloured dyes which find extensive applications in industry. Salts of carboxylic acids with amines are used as herbicides.

17.9. NITRO COMPOUNDS

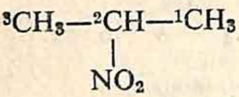
Nitro compounds are the nitro group ($-NO_2$ or $-N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$) substituted derivatives of alkanes or aromatic hydrocarbons. The aliphatic nitro compounds are called *nitroalkanes* while aromatic ones as *nitroarenes*.

They are named as the nitro derivatives of the hydrocarbons from which they are derived. The number of groups and their positions are indicated. Some examples are given below:

CH_3NO_2
Nitromethane

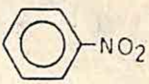
$CH_3CH_2NO_2$
Nitroethane

$^3CH_3-^2CH_2-^1CH_2NO_2$
1-Nitropropane

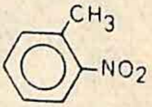


$$^3CH_3-\underset{\displaystyle NO_2}{\underset{|}{^2CH}}-^1CH_3$$

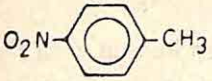
2-Nitropropane



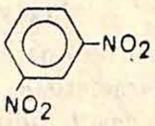
o-Nitrobenzene



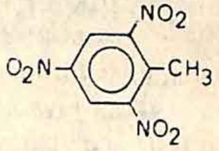
o-Nitrotoluene



p-Nitrotoluene



m-Dinitrobenzene



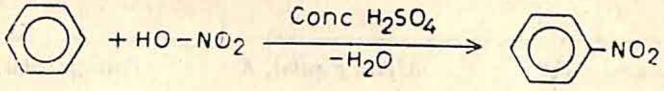
2,4,6-Trinitrotoluene

17.10. PREPARATION

Nitro compounds are generally prepared by direct nitration. A suitable nitrating mixture is employed depending on the nature of the compound to be nitrated and the extent to which it is to be nitrated.

Nitroarenes

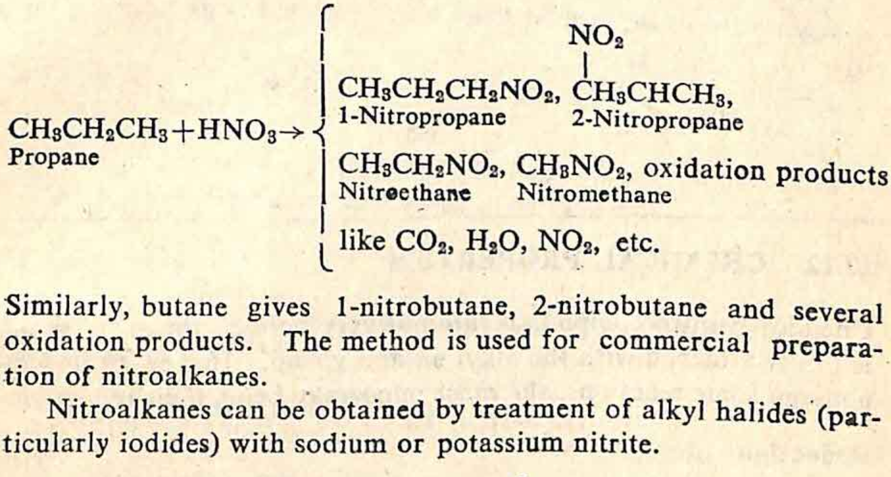
Aromatic nitro compounds are almost invariably prepared by direct nitration of the corresponding aromatic compound. For example, benezene, toluene, phenol, aniline, etc., can be easily nitrated using a nitrating mixture of concentrated nitric and sulphuric acids.



Benzene Nitrobenzene

Nitroalkanes

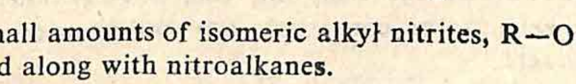
It is quite difficult to nitrate aliphatic hydrocarbons by the direct use of a nitrating mixture. High temperature nitration with nitric acid vapours yields many products. For example:



$$\underset{\text{Propane}}{CH_3CH_2CH_3} + HNO_3 \rightarrow \begin{cases} \underset{\text{1-Nitropropane}}{CH_3CH_2CH_2NO_2}, \ \underset{\text{2-Nitropropane}}{CH_3\overset{\overset{NO_2}{|}}{C}HCH_3}, \\ \underset{\text{Nitroethane}}{CH_3CH_2NO_2}, \ \underset{\text{Nitromethane}}{CH_3NO_2}, \text{ oxidation products} \\ \text{like } CO_2, H_2O, NO_2, \text{ etc.} \end{cases}$$

Similarly, butane gives 1-nitrobutane, 2-nitrobutane and several oxidation products. The method is used for commercial preparation of nitroalkanes.

Nitroalkanes can be obtained by treatment of alkyl halides (particularly iodides) with sodium or potassium nitrite.

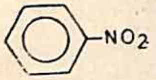
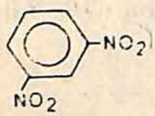
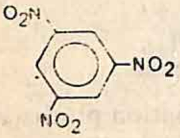


Small amounts of isomeric alkyl nitrites, R–O–N=O, are also formed along with nitroalkanes.

17.11. PHYSICAL PROPERTIES

Nitroalkanes are colourless liquids when pure and are pleasant smelling. They are sparingly soluble in water but dissolve readily in organic solvents. Most of them can be distilled smoothly at room temperature. Being polar, they have higher boiling points than the hydrocarbons of comparable molecular masses.

Aromatic nitro compounds are pale yellow in colour. Nitrobenzene is an oily liquid which boils at 483K and has a smell of bitter almonds. Nitroarenes are insoluble in water but soluble in organic solvents. They are generally volatile in steam. The melting and boiling points of nitro compounds increase with the number of nitro groups in the molecule. For example:

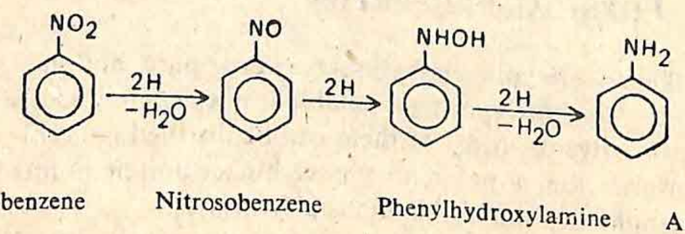
Nitro compound	*Melting point, K*	*Boiling point, K*
	279	483
	363	579
	395	—

17.12. CHEMICAL PROPERTIES

Chemically nitro compounds are not very active—the nitro group is firmly attached with the alkyl or aryl group. However, they do undergo some reactions, the most important being their reduction.

Reduction

Nitro compounds undergo reduction giving a variety of compounds depending on the reducing agent and the reaction conditions. For example, nitrobenzene can be converted into aniline or one of the intermediate products.



Nitrobenzene Nitrosobenzene Phenylhydroxylamine Aniline

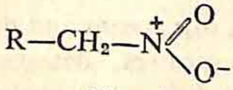
The intermediate products may also combine among themselves to form still more products.

Chemical reduction with strong reducing agent such as lithium aluminium hydride or a mixture of Fe, Sn or $SnCl_2$ with HCl as well as catalytic hydrogenation in presence of Ni or Pt convert nitro compounds into corresponding amines.

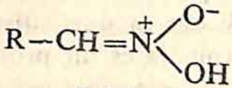
$$RNO_2+6H \longrightarrow RNH_2+2H_2O$$

Salt Formation

Primary and secondary nitroalkanes can exist as tautomeric mixtures of two forms—the *nitro form* and the *aci form.*

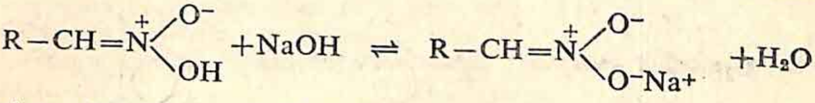


Nitro form



Aci form

The aci form, being a weak acid, can react with bases to form salts.



Tertiary nitroalkanes, $R_3C—NO_2$, cannot tautomerise to aci form and hence they do not react with bases to form salts.

Hydrolysis

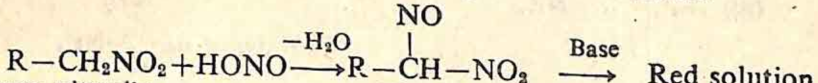
Primary nitroalkanes, on acid hydrolysis (with HCl or H_2SO_4), give carboxylic acids and hydroxylamine.

$$RCH_2NO_2+H_2O \xrightarrow{\text{Acid}} RCOOH+\underset{\text{Hydroxylamine}}{NH_2OH}$$

The method is used for the manufacture of hydroxylamine.

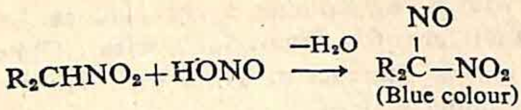
Reaction with Nitrous Acid

Primary, secondary and tertiary nitroalkanes react differently with nitrous acid. The reaction can, therefore, be used to distinguish the compounds from each other. A primary nitroalkane gives a nitroso derivative which has a tautomeric aci form called nitrolic acid. The acid dissolves in a base to give a red solution.



$$\underset{\text{Primary nitroalkane}}{R-CH_2NO_2}+HONO\xrightarrow{-H_2O}\underset{\text{Nitrolic acid}}{R-\overset{\overset{\displaystyle NO}{|}}{C}H-NO_2}\xrightarrow{\text{Base}}\text{Red solution}$$

A secondary nitroalkane also forms a nitroso derivative which is blue in colour. But this cannot tautomerise to aci form and thus remains insoluble in a base.



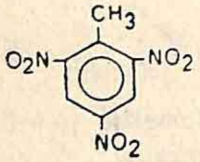
$$R_2CHNO_2 + HONO \xrightarrow{-H_2O} R_2\overset{\overset{NO}{|}}{C}-NO_2$$

(Blue colour)

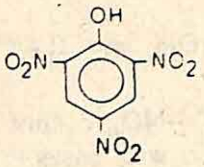
A tertiary nitroalkane does not react with nitrous acid because there is no hydrogen atom on the carbon atom carrying the nitro group. Thus the alkane remains colourless and unaffected.

17.13. USES OF NITRO COMPOUNDS

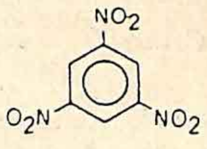
Nitro compounds are used as solvents for fats, oils, resins and dyes. They act as intermediates in production of explosives, detergents, medicines, etc. Many polynitro compounds such as trinitrotoluene (T.N.T.), picric acid and trinitrobenzene are unstable and are used as explosives. Nitrobenzene, which has an odour of almonds, is used in perfumes and flavourings. Its main use, however, is for the manufacture of aniline. Nitroalkanes find application in the production of hydroxylamine.



Trinitrotoluene (T.N.T.)



Picric acid

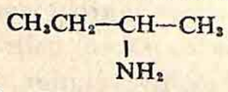


Trinitrobenzene

EXERCISES

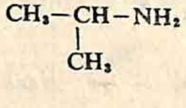
17.1 What are amines? How are they classified? Give examples.

17.2 Write the common names and IUPAC names of the following amines:

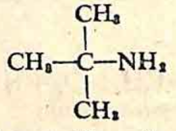
(i) 

$$CH_3CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

(ii) $CH_3CH_2CH_2NH_2$

(iii) 

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-NH_2$$

(iv) 

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-NH_2$$

17.3 Give examples of primary, secondary and tertiary aromatic amines.

17.4 Write short notes on:

(i) Gabriel's synthesis

(ii) Mendius reaction

(iii) Hofmann's bromamide reaction

17.5 Give industrial methods for the manufacture of (i) Aliphatic amines and (ii) Aniline.

17.6 Explain the following:
  (i) Why are lower amines soluble in water?
  (ii) Why are aliphatic amines more basic than ammonia?
  (iii) Why are aromatic amines less basic than ammonia?

17.7 How do aliphatic amines and aniline react with nitrous acid?

17.8 What is meant by exhaustive methylation?

17.9 What is Hofmann's elimination reaction? Explain its utility.

17.10 How are the following obtained from aniline:
  (i) Acetanilide (ii) Benzanilide (iii) Benzalanilide
  (iv) *p*-Benzoquinone (v) 2,4,6-Tribromoaniline

17.11 Why is the amino group in aniline protected before nitration? Explain the process of protecting the group.

17.12 Why does $-NH_2$ group activate the aromatic ring and at which positions?

17.13 Describe halogenation, sulphonation and nitration of aniline.

17.14 Give the tests of amines.

17.15 How are primary, secondary and tertiary amines distinguished?

17.16 Give the applications of amines.

17.17 What is Hinsberg's reagent? How does it react with different types of amines?

17.18 What are nitro compounds? Give the general formulae of nitroalkanes and nitroarenes.

17.19 Discuss the important reactions of nitro compounds.

17.20 How do nitroalkanes react with (i) alkalis, (ii) nitrous acid and (iii) hydrogen?

17.21 (i) Give the two tautomeric forms of nitroalkanes.
  (ii) How is nitrous acid used to distinguish primary, secondary and tertiary amines?

17.22 Give important uses of nitro compounds.

Unit 18

Polyfunctional Organic Compounds

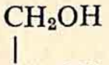
Preparation, properties and uses of glycol, glycerol oxalic acid and glycine.

In earlier Units, we have mainly studied compounds with one functional group. In this Unit, we will study some polyfunctional compounds which contain two or more functional groups, same or different. The functional groups present in a compound may interact mutually and impart entirely different properties to the molecule. We will pay special attention to such characteristics.

We start our study with the compounds containing functional groups of the same type. It will be followed by those in which the functional groups are different.

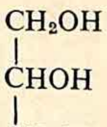
18.1. POLYHYDRIC ALCOHOLS

Polyhydric alcohols contain two or more alcoholic groups in their molecules. Two most important polyhydric alcohols are—ethylene glycol and glycerol.



$$\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$$

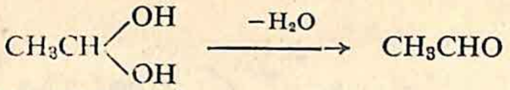
Ethylene glycol
(a dihydric alcohol)



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerol
(a trihydric alcohol)

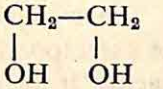
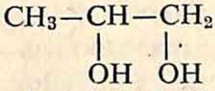
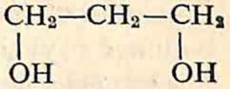
In polyhydric alcohols, more than one hydroxyl group cannot remain attached to the same carbon atom because this gives rise to an unstable arrangement. Such an arrangement undergoes a spontaneous change and loses a molecule of water. For example:



(Unstable arrangement)

18.2. ETHYLENE GLYCOL

Ethylene glycol (also called 1,2-ethanediol or simply glycol) is a prominent member of the class of dihydroxy alcohols known as *glycols*, *dihydric alcohols* or *diols*. Glycols with two hydroxyl groups attached to the adjacent carbon atoms are called 1, 2-glycols or *vicinal* glycols. In the common system, vicinal glycols are named after the olefins from which they are derived. When the two hydroxyl groups are situated at the extreme ends of a chain of carbon atoms, glycols are referred to as *polymethylene glycols*. These are named according to the number of methylene groups present in the molecule. In the IUPAC system, both the types of glycols are named as diols of parent alkanes and the positions of hydroxyl groups are shown by suitable numbers. Some examples are given below:

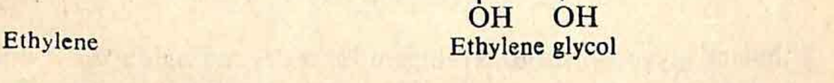
Formula:	 $\underset{OH}{CH_2}-\underset{OH}{CH_2}$	 $CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$	 $\underset{OH}{CH_2}-CH_2-\underset{OH}{CH_2}$
Common name :	Ethylene glycol	Propylene glycol	Trimethylene glycol
IUPAC name :	1, 2-Ethanediol	1, 2-Propanediol	1, 3-Propanediol

Preparation

Glycol is prepared by the following methods:

(i) HYDROXYLATION OF ETHYLENE

When ethylene is treated with Baeyer's reagent (cold dilute alkaline solution of potassium permanganate), hydroxylation takes place at both the carbon atoms.

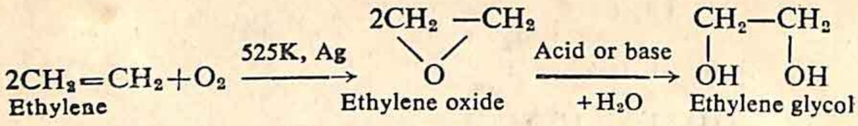


$$3CH_2=CH_2+2KMnO_4+4H_2O\longrightarrow 3\underset{OH}{CH_2}-\underset{OH}{CH_2}+2MnO_2+2KOH$$

Ethylene Ethylene glycol

(ii) HYDROLYSIS OF ETHYLENE OXIDE

Ethylene oxide (also called ethylene epoxide), obtained after catalytic oxidation of ethylene, is hydrolysed in the presence of a dilute acid or base to ethylene-glycol.

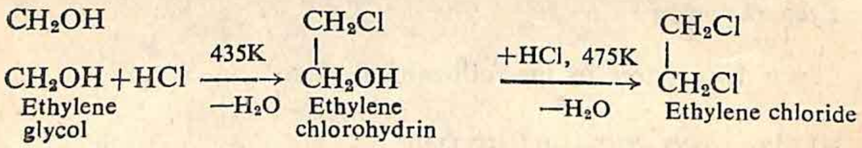


Physical Properties

Glycol is a colourless, sweet and viscous liquid. As it has two hydroxyl groups per molecule, it takes part in hydrogen bonding more effectively than a monohydroxy alcohol of comparable mass. This is evident from its high boiling point (470K) and miscibility in water and alcohol in all proportions. Ethylene glycol owes its use as an anti-freeze to its high boiling point, low freezing point and high solubility in water.

Chemical Properties

Glycol undergoes most of the reactions of primary alcohols like formation of ethers, esters, halides, etc. In such reactions, one or both hydroxyl groups react to form the corresponding compounds. For example, in reaction with halogen acids, it forms ethylene halohydrin and ethylene dihalide.

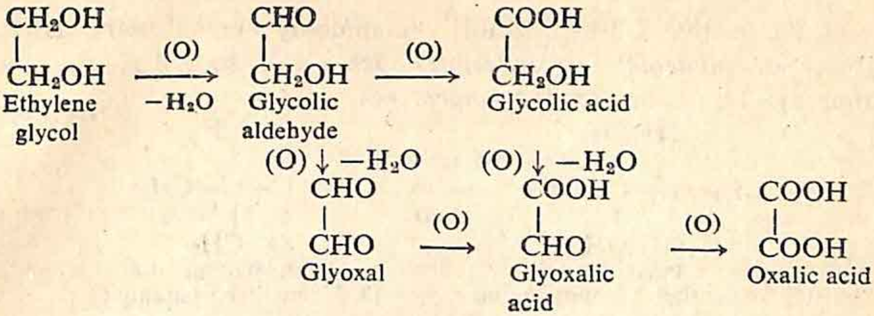


$$\underset{\text{Ethylene glycol}}{\begin{array}{l}CH_2OH\\ CH_2OH\end{array}} + HCl \xrightarrow[-H_2O]{435K} \underset{\text{Ethylene chlorohydrin}}{\begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array}} \xrightarrow[-H_2O]{+HCl,\ 475K} \underset{\text{Ethylene chloride}}{\begin{array}{l}CH_2Cl\\ |\\ CH_2Cl\end{array}}$$

In additon to these reactions, glycol gives certain characteristic reactions like oxidation, dehydration (pinacole-pinacolone rearrangement), etc.

OXIDATION

Ethylene glycol forms different products depending on the conditions of oxidation like the nature of oxidizing agent, temperature, etc. When oxidized with nitric acid, it forms a series of products and ultimately gives oxalic acid. The intermediate compounds can also be isolated.

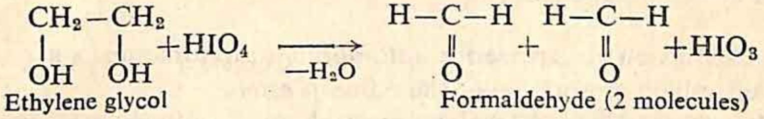


$$\underset{\text{Ethylene glycol}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} \xrightarrow[-H_2O]{(O)} \underset{\text{Glycolic aldehyde}}{\begin{matrix}CHO\\|\\CH_2OH\end{matrix}} \xrightarrow{(O)} \underset{\text{Glycolic acid}}{\begin{matrix}COOH\\|\\CH_2OH\end{matrix}}$$

$$(O)\downarrow -H_2O \qquad\qquad (O)\downarrow -H_2O$$

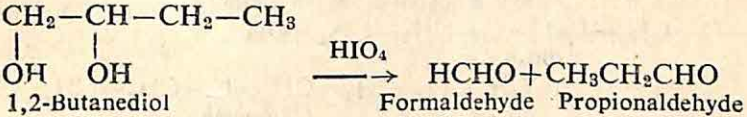
$$\underset{\text{Glyoxal}}{\begin{matrix}CHO\\|\\CHO\end{matrix}} \xrightarrow{(O)} \underset{\text{Glyoxalic acid}}{\begin{matrix}COOH\\|\\CHO\end{matrix}} \xrightarrow{(O)} \underset{\text{Oxalic acid}}{\begin{matrix}COOH\\|\\COOH\end{matrix}}$$

On oxidation with periodic acid, the cleavage of carbon-carbon bond occurs with the formation of formaldehyde.

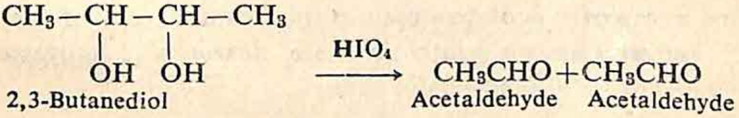


$$\underset{\text{Ethylene glycol}}{\begin{matrix}CH_2-CH_2\\|\quad\;\;|\\OH\;\;OH\end{matrix}} + HIO_4 \xrightarrow[-H_2O]{} \underset{\text{Formaldehyde (2 molecules)}}{\begin{matrix}H-C-H\\\|\\O\end{matrix} + \begin{matrix}H-C-H\\\|\\O\end{matrix}} + HIO_3$$

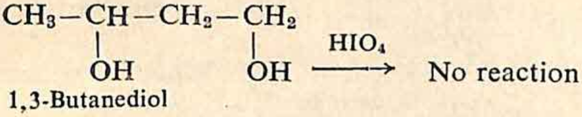
This oxidative cleavage is very useful in determination of the structure of the parent vicinal glycol since no two different glycols give the same combination of products. For example:



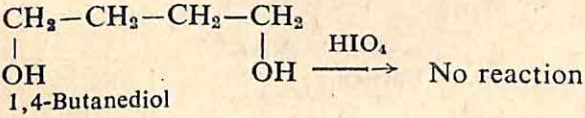
$$\underset{\text{1,2-Butanediol}}{\begin{matrix}CH_2-CH-CH_2-CH_3\\|\qquad\;|\qquad\qquad\qquad\\OH\quad OH\qquad\qquad\quad\end{matrix}} \xrightarrow{HIO_4} \underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Propionaldehyde}}{CH_3CH_2CHO}$$



$$\underset{\text{2,3-Butanediol}}{\begin{matrix}CH_3-CH-CH-CH_3\\|\qquad|\\OH\quad OH\end{matrix}} \xrightarrow{HIO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Acetaldehyde}}{CH_3CHO}$$



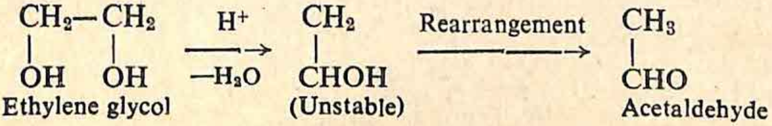
$$\underset{\text{1,3-Butanediol}}{\begin{matrix}CH_3-CH-CH_2-CH_2\\|\qquad\qquad\quad|\\OH\qquad\qquad OH\end{matrix}} \xrightarrow{HIO_4} \text{No reaction}$$



$$\underset{\text{1,4-Butanediol}}{\begin{matrix}CH_2-CH_2-CH_2-CH_2\\|\qquad\qquad\qquad\qquad|\\OH\qquad\qquad\qquad\quad OH\end{matrix}} \xrightarrow{HIO_4} \text{No reaction}$$

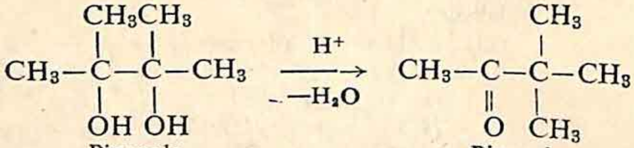
DEHYDRATION (PINACOLE-PINACOLONE REARRANGEMENT)

On treatment with dilute sulphuric acid under pressure in a sealed tube, ethylene glycol dehydrates and the product formed rearranges to give acetaldehyde.



$$\underset{\text{Ethylene glycol}}{\begin{matrix}CH_2-CH_2\\|\qquad|\\OH\quad OH\end{matrix}} \xrightarrow[-H_2O]{H^+} \underset{\text{(Unstable)}}{\begin{matrix}CH_2\\|\\CHOH\end{matrix}} \xrightarrow{\text{Rearrangement}} \underset{\text{Acetaldehyde}}{\begin{matrix}CH_3\\|\\CHO\end{matrix}}$$

2, 3-Dimethyl-2, 3-butanediol (commonly called tetramethyl glycol or *pinacole*) also undergoes such a dehydration giving 3,3-dimethyl-2-butanone (called *pinacolone*).



$$\begin{array}{c} CH_3\,CH_3 \\ |\quad\;| \\ CH_3-C-C-CH_3 \\ |\quad\;| \\ OH\;OH \end{array} \xrightarrow[-H_2O]{H^+} \begin{array}{c} \qquad CH_3 \\ \qquad | \\ CH_3-C-C-CH_3 \\ \|\quad\;| \\ O\quad CH_3 \end{array}$$

Pinacole
(2, 3-dimethyl-2, 3-butanediol)

Pinacolone
(3, 3-dimethyl-2-butanone)

The reaction is called *pinacole-pinacolone rearrangement*.

Uses of Ethylene Glycol

It is used as an antifreeze for automobile radiators and as a coolant for aeroplane motors under the name *prestone*.

Its ethers like *cellosolve*, *carbitol* and *diglyme* are excellent solvents for oils, fats, waxes, lacquers, enamels, etc.

$CH_3-CH_2-O-CH_2-CH_2-OH$

Cellosolve
(ethylene glycol monoethyl ether)

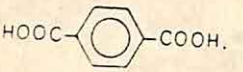
$C_2H_5-O-CH_2-CH_2-O-CH_2-CH_2-OH$

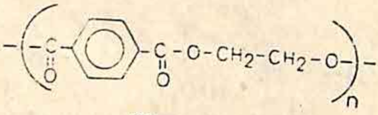
Carbitol

$CH_3-O-CH_2-CH_2-O-CH_2-CH_2-OCH_3$

Diglyme

Some esters of glycol are used in the manufacture of synthetic fibres. The well known synthetic fibre *dacron* is a polyester of ethylene glycol with terephthalic acid,

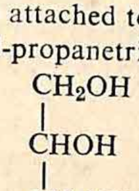




Dacron

18.3. GLYCEROL

Glycerol (commonly called glycerine) is a trihydric alcohol in which three hydroxyl groups are attached to three different carbon atoms. Its IUPAC name is 1, 2, 3-propanetriol.



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerol
(1, 2, 3-propanetriol)

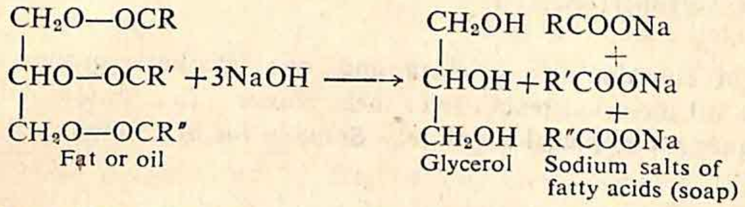
It occurs in oils and fats which are mixtures of esters of glycerol (glycerides) with higher fatty acids and unsaturated acids.

Preparation

Glycerol is obtained by the following methods:

FROM FATS AND OILS

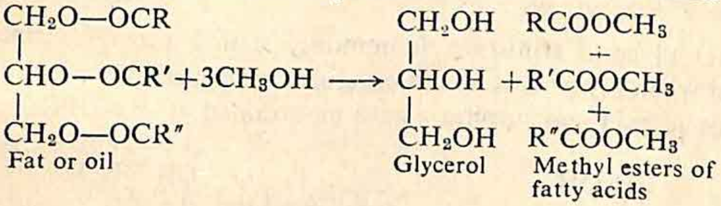
In soap manufacture, fats or oils are hydrolysed with sodium hydroxide when sodium salts of long chain fatty acids (called soaps) and glycerol are obtained. This process of hydrolysis is known as *Saponification.*



$$\begin{array}{l}CH_2O-OCR\\ |\\ CHO-OCR'\\ |\\ CH_2O-OCR''\end{array} + 3NaOH \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \begin{array}{c}RCOONa\\ +\\ R'COONa\\ +\\ R''COONa\end{array}$$

Fat or oil — Glycerol — Sodium salts of fatty acids (soap)

Glycerol can also be liberated from fats or oils by *trans-esterication* with methyl alcohol in presence of an acid or a base.

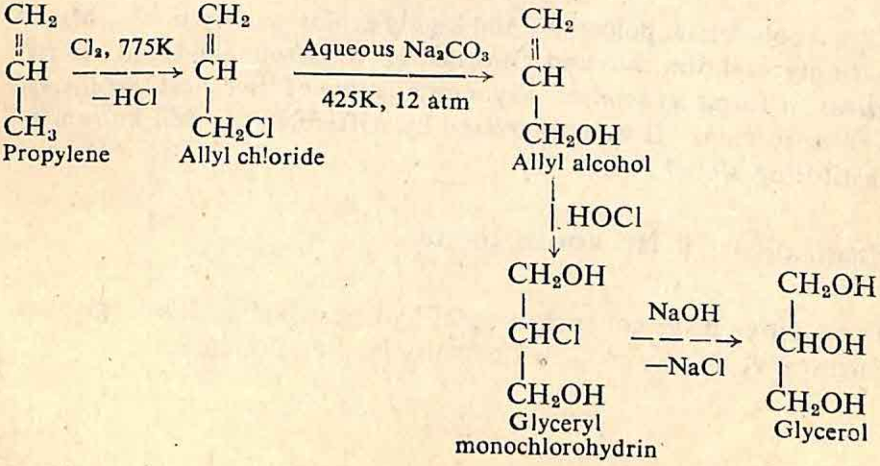


$$\begin{array}{l}CH_2O-OCR\\ |\\ CHO-OCR'\\ |\\ CH_2O-OCR''\end{array} + 3CH_3OH \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \begin{array}{c}RCOOCH_3\\ +\\ R'COOCH_3\\ +\\ R''COOCH_3\end{array}$$

Fat or oil — Glycerol — Methyl esters of fatty acids

FROM PROPYLENE

Glycerol is obtained on a large scale by hydration of propylene through the following series of reactions:



$$\begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_3\end{array} \xrightarrow[-HCl]{Cl_2,\ 775K} \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2Cl\end{array} \xrightarrow[425K,\ 12\ atm]{Aqueous\ Na_2CO_3} \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{array} \xrightarrow{HOCl} \begin{array}{l}CH_2OH\\ |\\ CHCl\\ |\\ CH_2OH\end{array} \xrightarrow[-NaCl]{NaOH} \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

Propylene — Allyl chloride — Allyl alcohol — Glyceryl monochlorohydrin — Glycerol

Propylene being obtained from cracking of petroleum, is quite cheap commercially.

Physical Properties

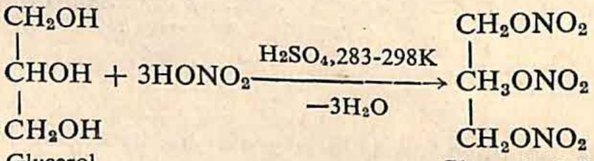
Glycerol is a colourless syrupy liquid, has a sweet taste and boils at 563K. It is soluble in water and alcohol in all proportions. When impure, it can be distilled with superheated steam under reduced pressure.

Chemical Properties

Glycerol contains two primary and one alcoholic groups and it gives all the usual reactions of these groups. In addition, it also undergoes some special reactions. Some of the important reactions are:

NITRATION

The ester glyceryl trinitrate (commonly called nitroglycerine) is obtained when glycerol is added carefully to a mixture of concentrated nitric acid and sulphuric acid maintained at 283-298K.



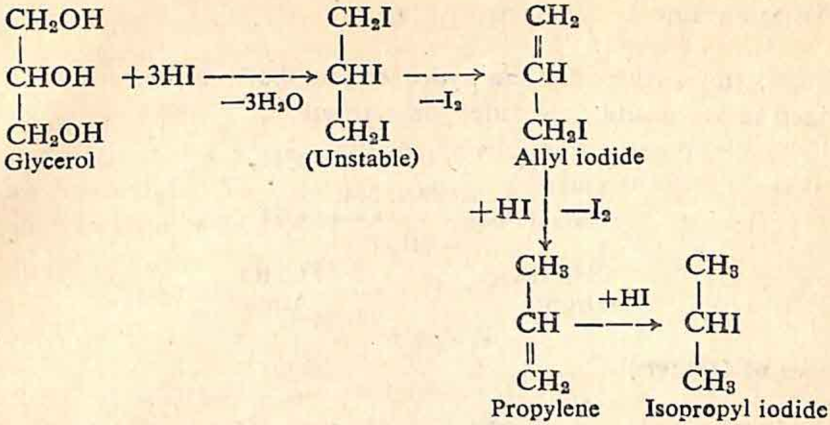
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3HONO_2 \xrightarrow[-3H_2O]{H_2SO_4, 283\text{-}298K} \begin{array}{l} CH_2ONO_2 \\ | \\ CH_3ONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

Glycerol Glyceryl trinitrate

It is a colourless, poisonous and highly explosive oily liquid. Mixed with glyceryl dinitrate and absorbed in a porous material *kieselguhar*, it forms *dynamite*. Dynamite is one of the best explosives known to man. It was discovered by Alfred Nobel, well known for instituting Nobel Prizes.

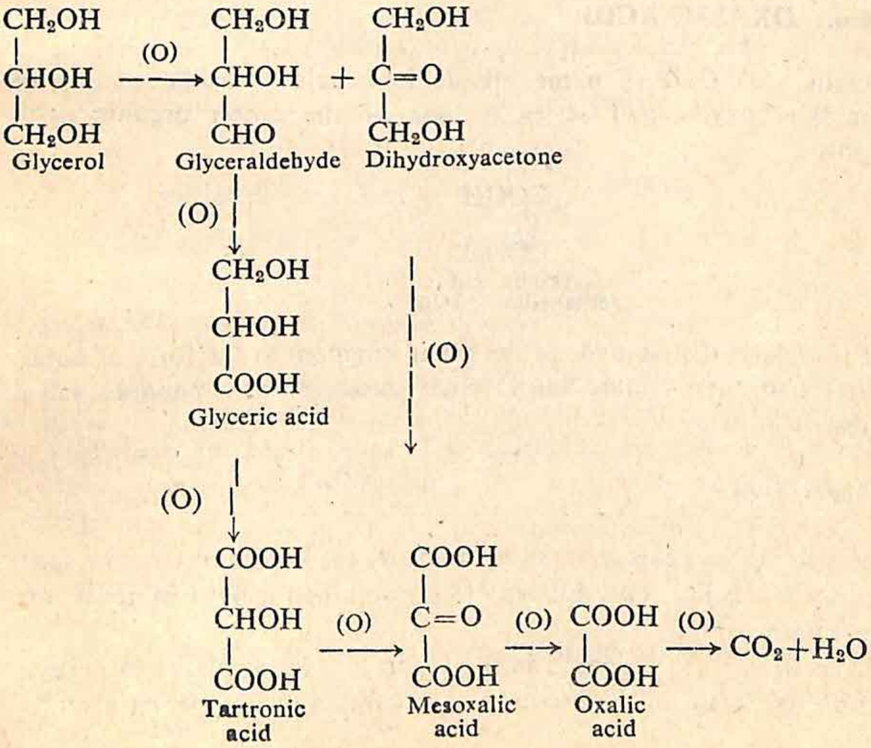
REACTION WITH HYDROGEN IODIDE

Depending on the concentration of hydrogen iodide used, glycerol forms allyl iodide, propene or finally isopropyl iodide.



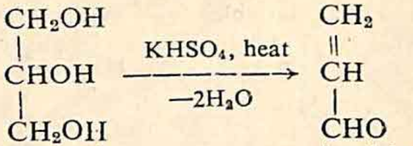
OXIDATION

With a mild oxidizing agent such as Fenton's reagent (hydrogen peroxide in the presence of ferrous sulphate), glycerol forms a mixture of glyceraldehyde (by oxidation of primary alcoholic group) and dihydroxyacetone (by oxidation of secondary alcoholic group). Stronger oxidizing agents can finally oxidize glycerol to carbon dioxide and water.



DEHYDRATION

On heating with potassium hydrogen sulphate, glycerol is dehydrated to an unsaturated aldehyde acrolein.



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} \xrightarrow[-2H_2O]{KHSO_4,\ heat} \begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CHO \end{matrix}$$

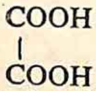
Glycerol Acrolein

Uses of Glycerol

Apart from its use in the manufacture of the explosive glyceryl trinitrate, glycerol has many applications. It is used in medicines (cough syrups, lotions, etc.), cosmetics, good quality soaps, toothpastes, non-drying inks, etc. Being hygroscopic, its covering prevents fruits from drying up. It is also used in tobaccos and cigarettes to prevent them from drying on exposure to air. A cross-linked polyester of glycerol with phthalic acid called *glyptal* is used as an alkyl resin.

18.4. OXALIC ACID

Oxalic acid (IUPAC name: ethanedionic acid), the first member of the dicarboxylic acid series, is one of the oldest organic acids known



$$\begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

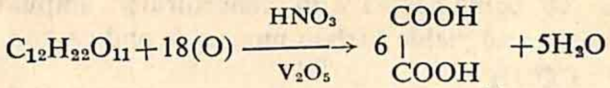
Oxalic acid
(ethanedionic acid)

It is widely distributed in the plant kingdom in the form of potassium hydrogen oxalate and calcium oxalate. Its ammonium salt is present in urine.

Preparation

Scheele (1776) prepared oxalic acid by the oxidation of cane sugar with nitric acid. Gay Lussac (1829) obtained it by fusion of saw dust with sodium hydroxide.

Oxalic acid is prepared in the laboratory by oxidizing cane sugar with nitric acid in the presence of vanadium pentoxide catalyst.

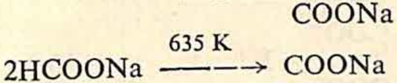


$$C_{12}H_{22}O_{11}+18(O)\xrightarrow[V_2O_5]{HNO_3}6\begin{array}{c}COOH\\|\\COOH\end{array}+5H_2O$$

Cane sugar Oxalic acid

Oxalic acid is manufactured starting with carbon monoxide and sodium hydroxide. The two react under pressure to form sodium formate which on being heated gives sodium oxalate.

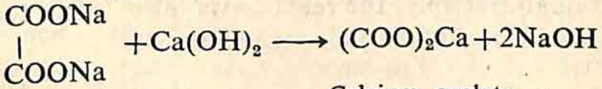
$$CO+NaOH\xrightarrow[10\text{-}15\ atm]{485\ K}HCOONa$$



$$2HCOONa\xrightarrow{635\ K}\begin{array}{c}COONa\\COONa\end{array}$$

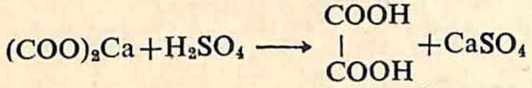
Sodium oxalate

The sodium salt is dissolved in water and treated with slaked lime when calcium oxalate is precipitated. The precipitate is filtered and treated with dilute sulphuric acid to obtain oxalic acid in solution. The solution is separated from the precipitated calcium sulphate and it is concentrated to obtain crystalline oxalic acid in the form of dihydrate, $\begin{array}{c}COOH\\|\\COOH\end{array}.2H_2O$.



$$\begin{array}{c}COONa\\|\\COONa\end{array}+Ca(OH)_2\longrightarrow(COO)_2Ca+2NaOH$$

Sodium oxalate Calcium oxalate



$$(COO)_2Ca+H_2SO_4\longrightarrow\begin{array}{c}COOH\\|\\COOH\end{array}+CaSO_4$$

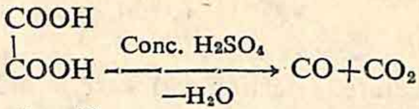
Calcium oxalate Oxalic acid

Physical Properties

Oxalic acid is a colourless, crystalline solid having two molecules of water of crystallization. It is soluble in water and alcohol but only sparingly soluble in ether. The hydrated acid melts at 374.5 K and loses water of crystallization. The anhydrous acid melts at 462.5K.

Chemical Properties

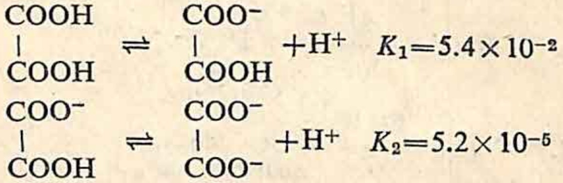
Oxalic acid contains two carboxyl groups and gives the usual reactions of carboxylic acids. It forms both normal and acid salts, esters, halides, amides, etc. However, it does not form any anhydride. On being heated with concentrated sulphuric acid, it gets dehydrated and yields carbon monoxide and carbon dioxide.



$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}\xrightarrow[-H_2O]{\text{Conc. } H_2SO_4} CO+CO_2$$

Oxalic acid

Being dibasic, it ionizes in two stages:

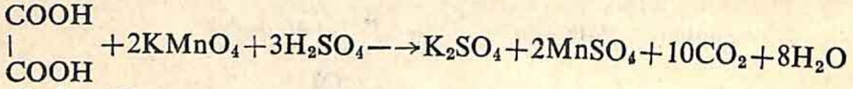


$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{COO^-}\\ |\\ \mathrm{COOH}\end{array} + H^+ \quad K_1=5.4\times10^{-2}$$

$$\begin{array}{l}\mathrm{COO^-}\\ |\\ \mathrm{COOH}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{COO^-}\\ |\\ \mathrm{COO^-}\end{array} + H^+ \quad K_2=5.2\times10^{-5}$$

The ionization of second carboxyl group takes place much less readily ($K_2=5.2\times10^{-5}$) than the ionization of first carboxyl group ($K_1=5.4\times10^{-2}$). This is because more energy is needed to remove a proton from the anion formed than from the uncharged oxalic acid molecule.

Oxalic acid decolorises a warm solution of acidfied potassium permanganate and itself is oxidized to carbon dioxide and water. The reaction is used for the detection of oxalate ions. As the acid is oxidized quantitatively, the reaction is also used for preparing standard solutions of potassium permanganate.



$$5\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}+2KMnO_4+3H_2SO_4 \longrightarrow K_2SO_4+2MnSO_4+10CO_2+8H_2O$$

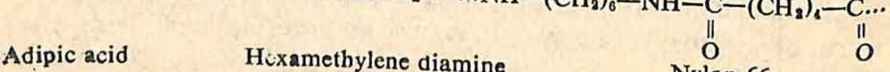
Oxalic acid

Uses of Oxalic Acid

Oxalic acid is used in volumetric titrations because of its quantitative reaction with potassium permanganate. It is also used for removing ink and rust spots.

Its antimony salts are used as mordants in dyeing and calico printing. Ferrous oxalate is used as a developer in photography.

Some of the higher homologues of oxalic acid also find many applications. Malonic acid, $HOOC-CH_2-COOH$ and its esters are important intermediates in several organic syntheses. Adipic acid, $HOOC(CH_2)_4COOH$, on reaction with hexamethylene diamine gives *nylon 66*, a very important material for making synthetic fibres.



$$HOOC(CH_2)_4COOH+NH_2(CH_2)_6NH_2 \rightarrow \ldots NH-(CH_2)_6-NH-\underset{\overset{\|}{O}}{C}-(CH_2)_4-\underset{\overset{\|}{O}}{C}\ldots$$

Adipic acid Hexamethylene diamine Nylon 66

18.5. GLYCINE

Glycine (also called amino acetic acid) is the simplest amino acid containing both the amino as well as carboxyl groups. Its IUPAC name is aminoethanoic acid. It has a sweet taste and was first obtained by the hydrolysis of glue and, therefore, it is also known as glycocoll (Greek: *glucus*=sweet, *kolla*=glue). It also occurs in the urine of horse as hippuric acid.

$$NH_2CH_2COOH$$

Glycine (amino acetic acid)
IUPAC name: Aminoethanoic acid

Preparation

Glycine is prepared by the following methods:

FROM CHLOROACETIC ACID

When concentrated ammonia solution reacts with chloroacetic acid, a mixture of glycine and ammonium chloride is obtained.

$$\underset{\text{Chloroacetic acid}}{CH_2ClCOOH}+2NH_3 \longrightarrow \underset{\text{Glycine}}{CH_2NH_2COOH}+HN_4Cl$$

Glycine and ammonium chloride have the same solubility. To separate the two, the solution is treated with cupric hydroxide when a deep blue complex of cupric aminoacetate (also called copper glycine) is formed. The complex is separated by fractional crystallization and its crystals are dissolved in water and decomposed by hydrogen sulphide.

$$\begin{tikzcd}
\underset{\text{Glycine}}{2CH_2NH_2COOH}+Cu(OH)_2 \arrow[r] & \underset{\text{Copper glycine}}{(CH_2NH_2COO)_2Cu}+2H_2O \arrow[d, "+H_2S"] \\
 & \underset{\text{Glycine}}{2CH_2NH_2COOH}+CuS
\end{tikzcd}$$

The precipitated cupric sulphide is filtered off and the filtrate is concentrated to obtain crystals of glycine.

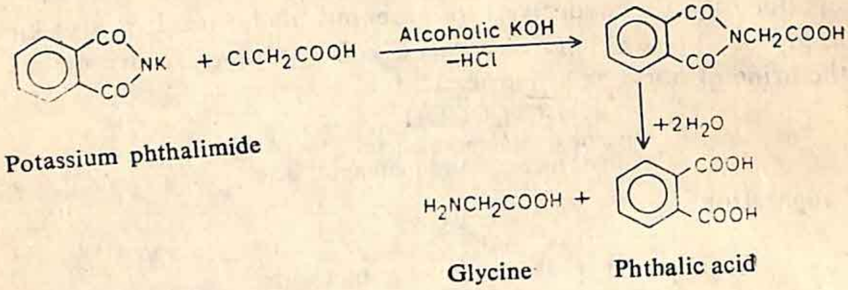
FROM FORMALDEHYDE (STRECKER'S SYNTHESIS)

In this method, formaldehyde is treated with ammonia and hydrogen cyanide followed by hydrolysis of the product,

$$\begin{tikzcd}
\underset{\text{Formaldehyde}}{HCHO}+NH_3 \arrow[r] & \underset{\text{Aldimine}}{CH_2=NH} + H_2O \arrow[d, "+HCN"] & \\
 & H_2NCH_2-CN \arrow[r, "2H_2O", "-NH_3"'] & \underset{\text{Glycine}}{H_2NCH_2COOH}
\end{tikzcd}$$

FROM POTASSIUM PHTHALIMIDE (GABRIEL'S PHTHALIMIDE SYNTHESIS)

The reaction consists in treating potassium phthalimide with chloroacetic acid followed by hydrolysis of the product formed.



Physical Properties

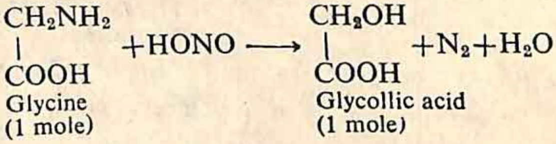
Glycine is a colourless, crystalline solid and has a sweet taste. It melts at 518 K with decomposition. It is freely soluble in water but insoluble in alcohol and ether.

Chemical Properties

In addition to the reactions typical to both amino and carboxyl groups, glycine gives some special reactions due to the presence of both the groups together in the molecule.

REACTIONS OF AMINO GROUP

(i) **With nitrous acid**. Glycine reacts with nitrous acid to form glycollic acid and liberates nitrogen.



$$\begin{array}{l} CH_2NH_2 \\ | \\ COOH \end{array} + HONO \longrightarrow \begin{array}{l} CH_2OH \\ | \\ COOH \end{array} + N_2 + H_2O$$

Glycine (1 mole) — Glycollic acid (1 mole)

The reaction is used for the estimation of amino acids and is known as *Van Slyke's method*.

(ii) **Acylation**. Glycine reacts with acetic anhydride or acetly chloride to form acetyl glycine.

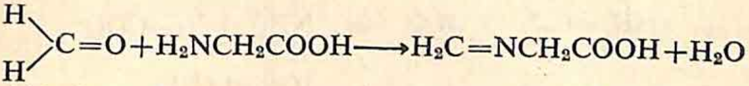
$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Glycine}}{NH_2CH_2COOH} \longrightarrow \underset{\text{Acetyl glycine}}{CH_3CONHCH_2COOH} + HCl$$

(iii) **Benzoylation.** Glycine undergoes benzoylation when treated with benzoyl chloride. The product formed is benzoyl glycine commonly known as *hippuric acid*. It is present in considerable amount in the urine of horse.

$$C_6H_5COCl + NH_2CH_2COOH \longrightarrow C_6H_5CONHCH_2COOH + HCl$$

Benzoyl chloride Glycine Hippuric acid

(iv) **With formaldehyde**. Glycine reacts with formaldehyde to give methylene glycine (also called aldimine).



$$\begin{matrix}H\diagdown\\ \quad C=O\\ H\diagup\end{matrix} + H_2NCH_2COOH \longrightarrow H_2C=NCH_2COOH + H_2O$$

Formaldehyde Glycine Aldimine

In aldimine, the amino group is blocked while its carboxyl group is free. Thus, it can be conveniently titrated against an alkali using phenolphthalein indicator. The titration is referred to as *Sorenson's formal titration*.

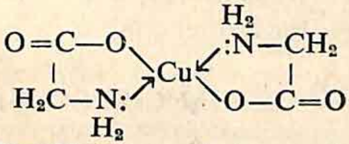
REACTIONS OF CARBOXYL GROUP

(i) **Salt formation**. Glycine forms salts with bases. For example:

$$H_2NCH_2COOH + NaOH \longrightarrow H_2NCH_2COONa + H_2O$$

Glycine Sodium salt of glycine

Deep blue colour of copper salt of glycine is like that of copper-ammonia complex. Here, too, the coordination takes place with the amino group.



Deep blue copper-glycine complex

(ii) **Decarboxylation**. When heated with barium hydroxide solution, glycine is decarboxylated to methylamine.

$$H_2NCH_2COOH + Ba(OH)_2 \longrightarrow CH_3NH_2 + BaCO_3 + H_2O$$

Glycine Methylamine

(iii) **With alcohols**. Glycine forms esters with alcohols. For example:

$$H_2NCH_2COOH + C_2H_5OH \longrightarrow H_2NCH_2COOC_2H_5 + H_2O$$

Glycine Ethyl amino acetate

In the ester formation, the carboxyl group is blocked while amino remains free. Thus, esters of glycine are distinctly basic in character.

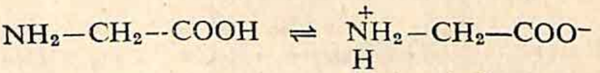
(iv) **With phosphorus pentachloride**. Glycine reacts with phosphorus pentachloride to form acid chloride.

$$H_2NCH_2COOH + PCl_5 \longrightarrow H_2NCH_2COCl + POCl_3 + HCl$$

Glycine Amino acetly chloride

INTERNAL SALT FORMATION

In the glycine molecule, the basic amino group and the acidic carboxyl group interact with each other to form a sort of dipolar *'internal salt'* known as *zwitter ion.*



$$NH_2-CH_2--COOH \rightleftharpoons \underset{H}{\overset{+}{N}}H_2-CH_2-COO^-$$

(Zwitter ion)

The presence of zwitter ion is evident from the following facts :

Glycine melts at a high temperature (518K with decomposition) showing the existence of large intermolecular forces arising due to electrostatic attractions of dipolar ions.

Very low solubility of glycine in organic solvent indicates its polar character. It is freely soluble in water. Its aqueous solution shows high dipole moment.

The acidity constant ($K_a=1.6\times10^{-10}$) and basicity constant $K_b=2.5\times10^{-12}$) for glycine are low consistent with the zwitter ion character. In the zwitter ion structure, the acid centre is substituted ammonium ion ($H_3\overset{+}{N}-$) and the basic centre is carboxylate ion ($-COO^-$). The ion may lose or gain a proton depending upon the conditions. In aqueous solution, glycine tends to lose a proton and the amino acid anion predominates over the zwitter ion.

$$H_3\overset{+}{N}CH_2COO^-+H_2O \rightleftharpoons H_2NCH_2COO^-+H_3O^+$$

(Amino acid anion predominates)

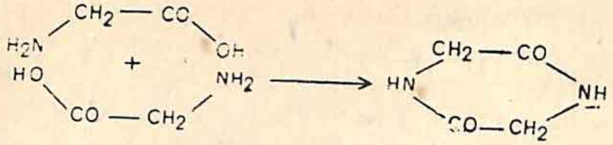
In an electric field, the anion moves towards anode. In presence of an acid, zwitter ion accepts a proton and becomes a cation.

$$H_3\overset{+}{N}CH_2COO^-+H^+ \rightleftharpoons H_3\overset{+}{N}CH_2COOH$$

The cation moves towards cathode during electrolysis.

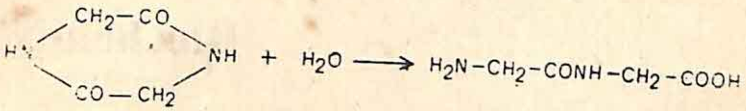
Thus, glycine forms an anion or cation depending on the hydrogen ion concentration of the solution. At pH 6, it has equal tendency to acquire either of the two forms. Its charge becomes zero at this pH and it does not migrate under the influence of an electric field. This pH is referred to as the *isoelectric point* of glycine. Other amino acids also possess their characteristic isoelectric points.

Because of this interaction of the two groups present together in the molecule, glycine gives some special reactions such as *internal diamide formation.* On being heated, glycine loses water to form a cyclic diamide called diketopiperazine.



Glycine (2 molecules) Diketopiperazine

The partial hydrolysis of diketopiperazine yields an open chain amide—the dipeptide of glycine.



Diketopiperazine

Glycyl glycine
(dipeptide of glycine)

EXERCISES

18.1 What are polyfunctional compounds? What is the special characteristic feature of their chemical behaviour?

18.2 Give one example each of a dihydric alcohol and a trihydric alcohol. How are they prepared?

18.3 What are vicinal glycols? How is 1,2-ethanediol prepared?

18.4 How is periodic acid used in determining the structures of glycols?

18.5 Why is glycol used as an antifreeze? Give its important uses.

18.6 (i) What is the IUPAC name of glycerol?
(ii) How is glycerol obtained from fats?
(iii) Give important uses of glycerol?

18.7 How will you obtain glycerol starting with propylene?

18.8 How are the following obtained from glycerol :
(i) Glyceryl nitrate (ii) Propene
(iii) Tartronic acid (iv) Acrolein

18.9 What are the products formed when glycerol is oxidized with Fenton's reagent? How is dynamite obtained from glycerol?

18.10 How is oxalic acid manufactured? Give its important reactions.

18.11 How will you detect and determine oxalic acid present in a solution?

18.12 What happens when oxalic acid is heated with concentrated sulphuric acid? Give important uses of the dicarboxylic acid.

18.13 What is the IUPAC name for glycine? Give its methods of preparation.

18.14 Write short notes on the following:
(i) Pinacol-pinacolone rearrangement (ii) Saponification
(iii) Gabriel's phthalimide synthesis (iv) Zwitter ion

18.15 Why does glycine form an internal salt? Explain the significance of isoelectric point.

18.16 What happens when glycine is heated and the product obtained is hydrolysed?

18.17 Give typical reactions of glycine with special reference to internal diamide formation.

Unit 19

Biochemistry

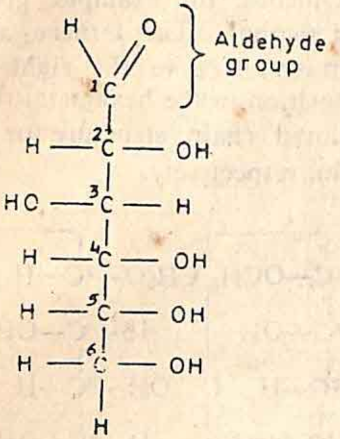
General treatment of carbohydrates, lipids, vitamins, hormones, proteins and nucleic acids (DNA and RNA).

Biochemistry is the science that deals with the chemistry of life processes which depend on chemical reactions. The living organisms have highly complex chemical structures and they undergo biological functions such as reproduction, movement, thinking, growth and ageing. In the composition of all the living systems and in their functioning, several complex life-less organic compounds referred to as *biochemicals* play vital and specific roles. In this Unit, we shall consider important groups of these biosubstances such as carbohydrates, lipids, vitamins, hormones, proteins, enzymes and nucleic acids.

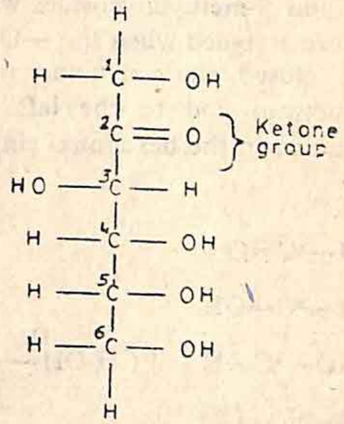
19.1. CARBOHYDRATES

Carbohydrates may be considered as the hydrates of carbon with the general formula, $C_x(H_2O)_y$ (where x and y are the whole numbers). When the number of carbon atoms lies between 3 and 7, the carbohydrates are called simple sugars or *monosaccharides*. A monosaccharide with 3-carbon atoms is called a triose; one with 4 carbons is called a tetrose; with 5 carbons, a pentose; with 6 carbons, a hexose and with 7 carbons, a heptose. Chemically, a carbohydrate is either a polyhydroxy aldehyde (e.g., glucose), a polyhydroxy ketone (e.g., fructose), or a substance which on hydrolysis yields at least one of these polyhydroxy compounds. The aldehydic sugars are collectively referred to as *aldoses* and the ketonic sugars, *ketoses*.

These names may be coupled with the terms indicating the number of carbon atoms in the molecule. Thus, glucose which contains 6-carbon atoms (i.e., hexose) and an aldehyde group (i.e., aldose) is called an *aldohexose*. Similarly, fructose acquires the name *ketohexose* because it contains a ketone group and 6 carbons.

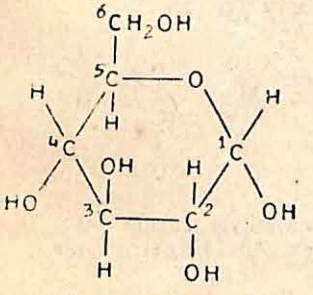


glucose (a polyhydroxy aldehyde, an aldohexose)

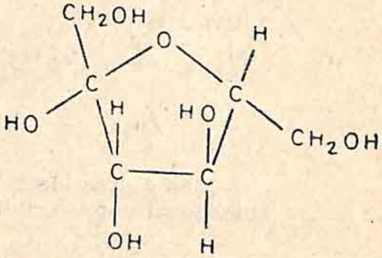


Fructose (a polyhydroxy ketone, a ketohexose)

Though the carbohydrates may be represented as *open chain* compounds (as shown above), there is sufficient evidence to support the view that they exist in the less active but more common form of a *closed ring* or *cyclic* structure. In the body, there is an equilibrium between the two forms. The cyclic structures of glucose and fructose are represented as:

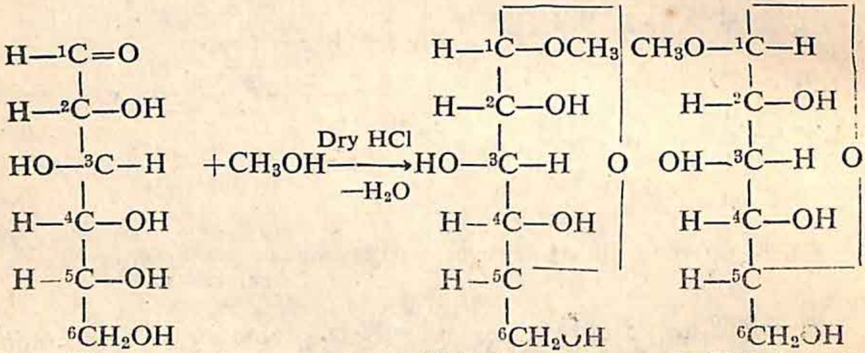


Glucose (cyclic structure)

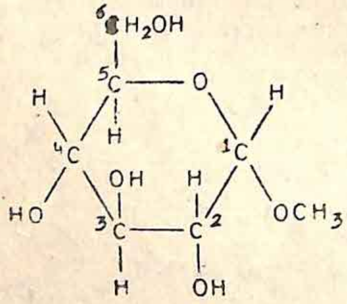


Fructose (cyclic structure)

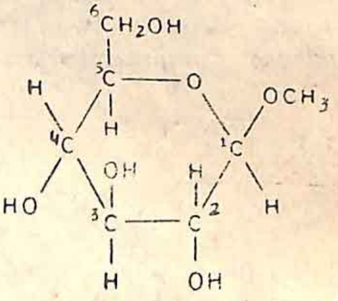
Glucose, fructose and galactose are the three most important monosaccharides which make up the bulk of carbohydrates. All the monosacchrides are soluble in water, char on heating and do not get hydrolyzed. They possess a sweet taste. Rating sucrose (cane sugar) as 100, the values for relative sweetness of some common sugars like lactose, maltose, glucose, invert sugar and fructose are 16, 33, 74, 130 and 173, respectively. Monosaccharides undergo characteristic reactions of alcohols and of aldehydes or ketones. In presence of dry HCl, they react with alcohols or phenols to form the products known as *glycosides*. Glucose, for example, gives α- and β-methylglycosides with methyl alcohol. The terms α- and β- are assigned when the —OCH_3 group is written to the right of the closed chain structure (or down position in the hexagonal ring structure) and to the left of the closed chain structure (or up position in the hexagonal ring structure), respectively.



Glucose α Methylglycoside β- Methylgycoside
(closed chain structures)

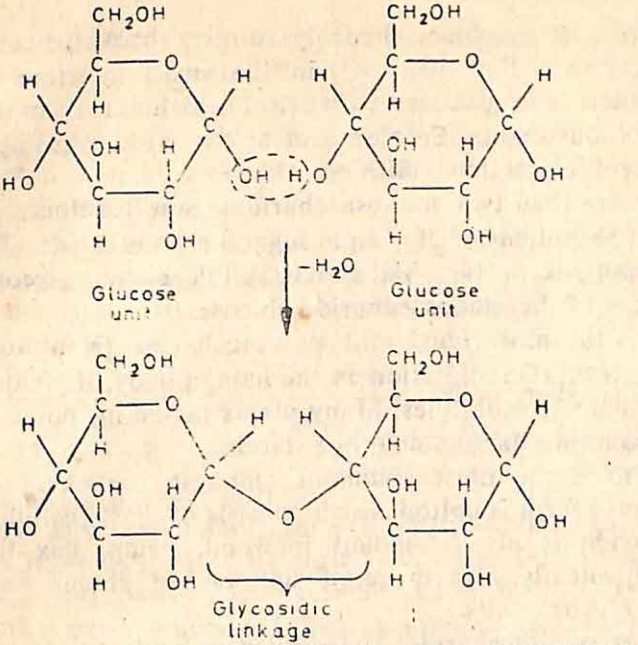


α- Methylglycoside
(hexagonal ring structure)

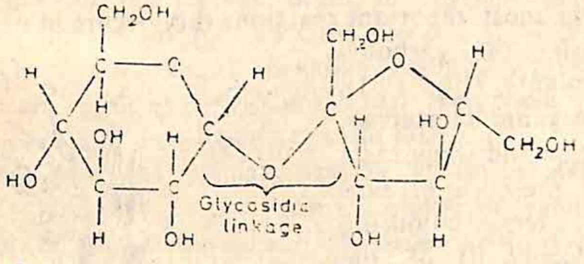


β- Methylglycoside
(hexagonal ring structure)

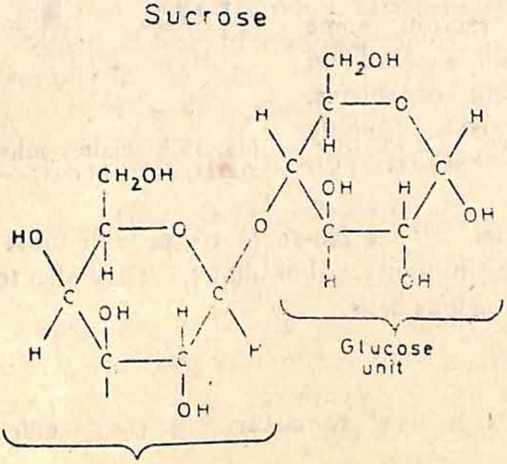
When two identical or different monosaccharides join together by elimination of a water molecule, a new carbohydrate called a *disaccharide* is obtained. For example, two glucose molecules form the disaccharide maltose. Similarly, the disaccharide sucrose is obtained by combination of glucose and fructose, and the disaccharide lactose results when glucose combines with galactose.



Maltose



Sucrose



Disaccharides on being hydrolyzed give back the component monosaccharides. For instance, in the small intestine enzymes hydrolyze sucrose to glucose and fructose which are then absorbed into the bloodstream. Sucrose can also be hydrolyzed by boiling water under mild acidic conditions.

When more than two monosaccharides join together, *polysaccharides* (i.e. polymers of simple sugars) are obtained. The most important polysaccharides, viz. starch, cellulose and glycogen, are the polymers of the monosaccharide glucose.

Starch is the most important polysaccharide from nutritional point of view. On digestion in the human body, it yields a large number of glucose molecules. Many plants including potatoes, rice and corn contain a large amount of starch.

Cellulose is the most abundant amongst carbohydrates. Its purest natural form is cotton which consists of 95% cellulose. The polysaccharide is also abundant in wood, hemp, flax, linen and paper. Chemically, it is made of unbranched chains containing 1800-3000 glucose units.

Glycogen polysaccharide, often called animal starch, exists in the liver and muscles of animals. The molecule is very large and extensively branched. Its molecular weight may exceed 3 million.

One of the most important reactions that occurs in nature is the *photosynthesis* of carbohydrates by plants (Fig. 19.1). Simple inorganic substances, carbon dioxide and water react together in presence of sunlight and green colouring matter (chlorophyll) of the plant and produce sugars. Through this reaction, some energy of the sun is stored and used by living organisms. Moreover, the oxygen supply of the atmosphere is also replenished.

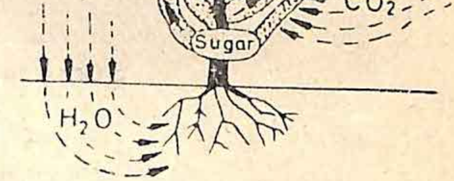


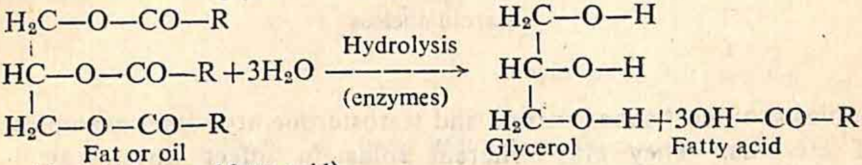
Fig. 19.1. Photosynthesis of carbohydrates, $6CO_2+6H_2O \longrightarrow C_6H_{12}O_6+6O_2$.

Carbohydrates act as *bio-fuels* to provide most of the energy required for life (in plants and animals). They also form structural components of various cells.

19.2. LIPIDS

The term *lipids* is used to cover fats (fatty acid esters) and a variety of other compounds like *phospholipids*, *steroids*, etc., which occur in living organisms. They are soluble in organic solvents such as ether, chloroform and carbon tetrachloride but seldom in water. Lipids may not have same functional groups and are not polymerized. Their molecular weights are relatively low and they have similarities with hydrocarbons.

The common fats and oils are the triglyceride esters of fatty acids. The esters on enzymatic digestion in the body (i.e. hydrolysis), give one molecule of glycerol and three molecules of fatty acid.



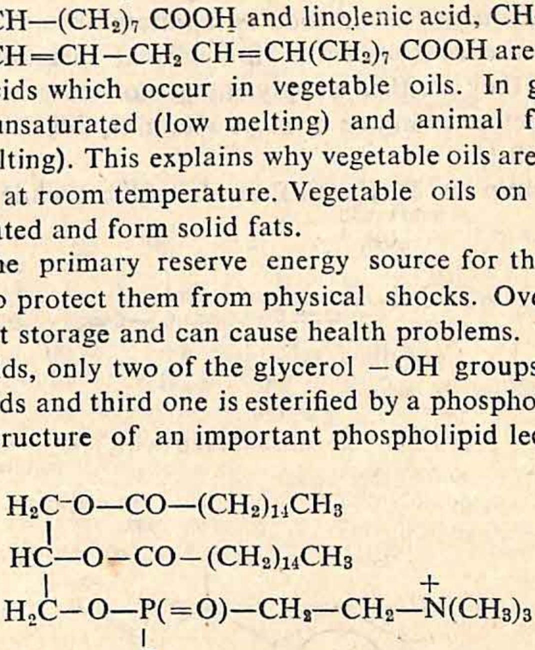
$$\begin{array}{lcl} H_2C-O-CO-R & & H_2C-O-H \\ | & & | \\ HC-O-CO-R+3H_2O & \xrightarrow[\text{(enzymes)}]{\text{Hydrolysis}} & HC-O-H \\ | & & | \\ H_2C-O-CO-R & & H_2C-O-H+3OH-CO-R \\ \text{Fat or oil} & & \text{Glycerol} \qquad \text{Fatty acid} \end{array}$$

(triglyceride ester of fatty acid)

The most common saturated fatty acids, viz., stearic acid, $CH_3(CH_2)_{16}COOH$ and palmitic acid, $CH_3(CH_2)_{14}COOH$, and unsaturated fatty acid, i.e., oleic acid, $CH_3(CH_2)_7-CH=CH-(CH_2)_7COOH$ occur in animals and plants. Linoleic acid, $CH_3(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_7COOH$ and linolenic acid, $CH_3CH_2-CH=CH-CH_2-CH=CH-CH_2CH=CH(CH_2)_7COOH$ are the unsaturated fatty acids which occur in vegetable oils. In general, vegetable oils are unsaturated (low melting) and animal fats are saturated (high melting). This explains why vegetable oils are liquids and fats are solids at room temperature. Vegetable oils on hydrogenation get saturated and form solid fats.

Fats act as the primary reserve energy source for the living organisms and also protect them from physical shocks. Overeating results in excess fat storage and can cause health problems.

In phospholipids, only two of the glycerol $-OH$ groups are esterified by fatty acids and third one is esterified by a phosphoric acid derivative. The structure of an important phospholipid lecithin is shown below:

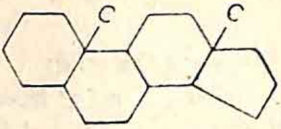


$$\begin{array}{l} H_2C-O-CO-(CH_2)_{14}CH_3 \\ | \\ HC-O-CO-(CH_2)_{14}CH_3 \\ | \\ H_2C-O-P(=O)-CH_2-CH_2-\overset{+}{N}(CH_3)_3 \\ \qquad\qquad | \\ \qquad\qquad O- \end{array}$$

Lecithin

Phospholipids are found in egg yolk. Being present in more active tissues of the body and in the blood, they play an important role in the structure and functioning of nerve tissues.

Steroid lipids are completely different from fats and phospholipids. They have a characteristic cyclic structure with the basic nucleus (called the steroid nucleus) shown below:



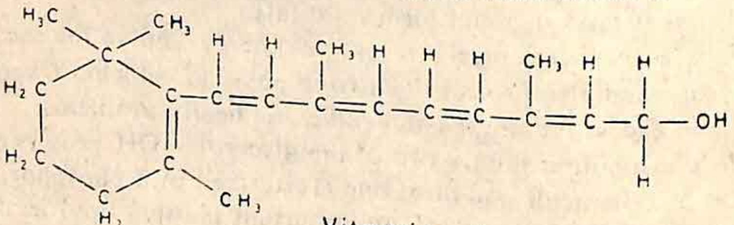
Steroid nucleus

Cholesterol, cortisone, estrone and testosterone are some examples of steroids. They play different roles to affect physiological activity—some function as vitamins and hormones.

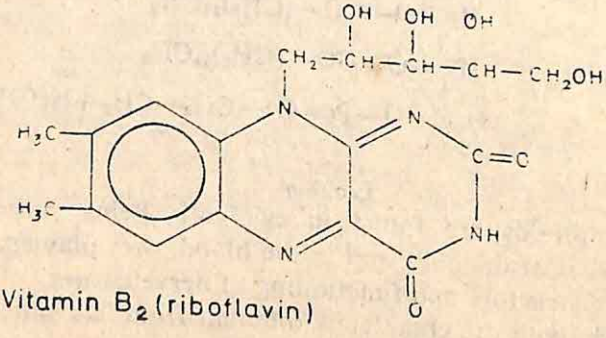
19.3. VITAMINS

Vitamins, as the name suggests, are 'vital' or necessary for life. They are comparatively simple organic substances that are required in small quantities in food to maintain normal growth and health. Their presence is essential for normal metabolism of body cells though they neither supply energy nor serve as building material. If the diet lacks in one or more vitamins, deficiency disease results (Table 19.1).

Vitamins A, D, K and E are fat-soluble while others are water-

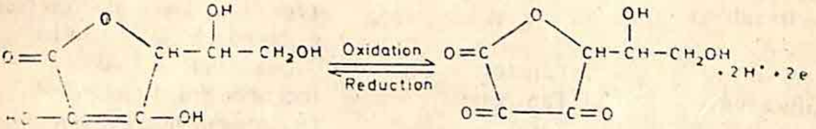


Vitamin A



Vitamin B_2 (riboflavin)

soluble. The fat-soluble vitamins can accumulate in the body and their excess may cause problems. However, if the water-soluble vitamins exceed the requirements of the body, they are excreted in the urine. Common vitamins together with their dietary sources and results of deficiency are listed in Table 19.1. The structures of vitamins A, B_2 and C are shown below:



Ascorbic acid
(vitamin C)

Dehydroascorbic acid

TABLE 19.1 : Some Important Vitamins

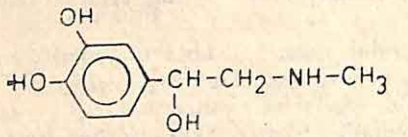
Vitamin	*Dietary source*	*Deficiency-result*
A	Green and yellow vegetables (carrots, pumpkins, tomatoes, etc.), egg yolk, butter, milk, codliver oil	Night blindness, eye disease—xerophthalmia, drying up/of skin xerosis
B_1 (thiamine)	Yeast, cereal grains, nuts, legumes, organ meats, rice polishings, milk, vegetables	Loss of appetite and energy, beriberi disease
B_2 (riboflavin)	Milk, leafy vegetables, yeast, lean meats, eggs, cheese, legumes	Skin disorder, tongue swollen, cracked lips
B_6 (pyridoxine)	Cereals, yeast, liver, legumes	Skin and nerve disturbances
B_{12} (cyanocobalamine)	Meat, liver, eggs	Anaemia
C (ascorbic acid)	Citrus fruits (oranges, lemons amla, tomatoes, chillies, papita, etc.), green vegetables	Scurvy disease (weight loss, painful joints, gums bleed)
D	Fish liver oils, made in the body by the action of sunlight	Rickets in children
E (tocopherol)	Leafy vegetables, wheat germ and cottonseed oils	Sterility in rats, degeneration of muscle fibres in animals
K	Leafy vegetables (spinach, cabbage, etc.), egg yolk, yeast, liver	Impaired clotting of blood

19.4. HORMONES

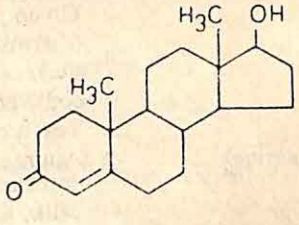
Hormones are chemical substances which are produced by endocrine glands. These glands are often called ductless glands because their products, the hormones, are secreted directly into the bloodstream. Each hormone usually exerts a specific effect on a certain type of cell or organ to help metabolic processes. Some important hormones with their sources and major functions are given in Table 19.2.

TABLE 19.2: Some Important Hormones

Hormone	*Source of secretion*	*Principal function*
Thyroxine	Thyroid	Stimulates metabolism
Epinephrine (adrenaline)	Adrenal medulla	Increases pulse rate and blood pressure, releases glucose from glycogen and fatty acid from fats
Insulin	Pancreas	Decreases blood glucose
Glucagon	Pancreas	Increases blood glucose
Testosterone	Testis	Develops male sex organs
Estrogen	Ovary	Influences development of female sex organs
Progesterone	Ovary	Prepares unterus for pregnancy, affects menstural cycle



Epinephrine (adrenaline)

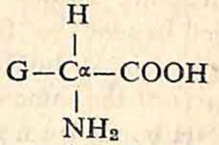


Testosterone

19.5. Proteins

Proteins are complex nitrogenous compounds and are the structural units of animal tissues, just as cellulose is the constituent of plant cells. They also occur in all plants especially in seeds. They are the essential parts of our diet and are vital for the maintenance and growth of life. The name protein is derived from the Greek word *proteios* meaning first or primary, *i.e.*, compounds of primary importance. They contain the elements carbon, hydrogen, nitrogen, oxygen and sometimes sulphur and phosphorus. Animals derive prot ins from plants as their food. The latter, of course, build their proteins from carbon dioxide, water, soil, minerals (ammonium salts, nitrates) and sunlight. During digestion the plant proteins are hydrolyzed in the body by enzymes into amino acids which are absorbed by blood and reach various tissues. Hence animal proteins are synthesized from amino acids. They are polyamides and the monomers from which they are derived are α-amino acids. A single protein molecule may contain hundreds or even thousands of these amino acid units. Twenty six amino acids are known which combine differently to give protein molecules. It is likely that tens of thousands of these proteins are required to make up and run an animal body and this set of proteins is not indentical with the proteins required for another type of animal.

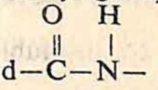
The general formula of an amino acid is

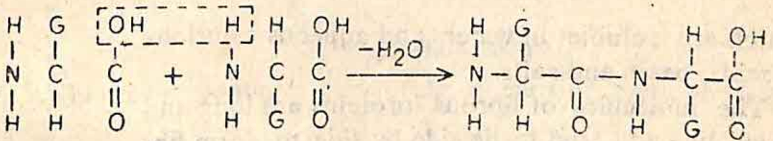


$$G-\underset{\displaystyle NH_2}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C^{\alpha}}}}}-COOH$$

where $-NH_2$ and $-COOH$ are amino group and carboxyl group, respectively. G is a group which differs in different amino acids. The simplest amino acid is glycine where $G=H$. If $G=CH_3$, the amino acid is alanine, CH_3CHNH_2COOH. All α-amino acids, except glycine, contain an asymmetric carbon atom and, therefore, show optical activity.

Peptide Linkage

In proteints, the adjacent amino acids are joined in such a way that the amino group of one acid joined with the carboxyl group of its neighbour forms an imide bond. The imide bond  $-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-$ in proteins is called *peptide bond*.



Dipeptide

Depending on the number of amino acid residues per molecule, they are known as dipeptides, tripeptides, and so on finally polypeptides. By convention, peptides of molecular weight up to 10,000 are known as *polypeptides* and those with higher than 10,000 are called *proteins*.

Primary Structure of Proteins

It is clear from the structure of a polypeptide (shown below) that every third atom of the peptide chain is attached to side chain G the structure of which depends upon the particular amino acid residue involved. This structure of the polypeptide is the primary structure of proteins. A line drawn connecting the G groups (as shown below) would resemble a helical or a spiral structure.

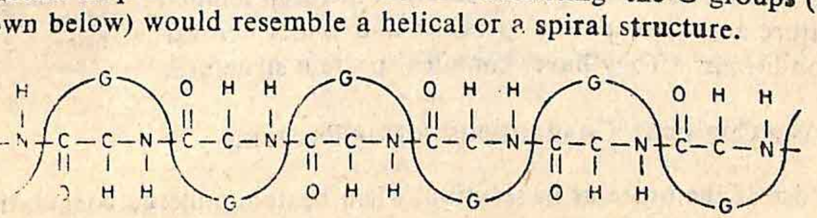


Fig. 19.2. Structure of a polypeptide indicating a helical structure.

Secondary Structure of Proteins

This structure shows the way in which the polypeptide chains are arranged in space to form *coils*, *sheets* or *compact spheroids* with hydrogen bonds holding different chains or different parts of the same chain (Fig. 19.3). The C=O and—NH bonds form strong hydrogen bonds which link one part of the chain to another. Each chain is coiled to form a right-handed spiral called an α-helix. On an average there are 3.7 amino acid residues per turn of the coil.

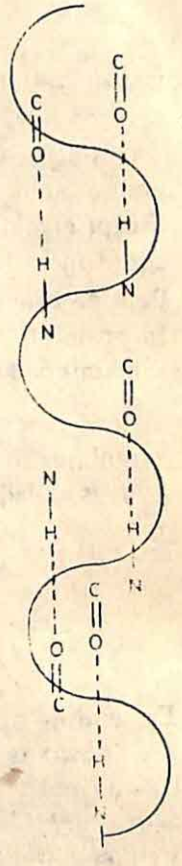


Fig. 19.3 A portion of a polypeptide chain coiled into an α-helix in which hydrogen bonds are linking the loops of the helix.

Classification of Proteins

Proteins are divided into two broad classes:

(i) FIBROUS PROTEINS

Which are insoluble in water and

(ii) GLOBULAR PROTEINS

Which are soluble in water and aqueous solutions of acids, bases and salts.

The molecules of fibrous proteins are long and thread-like and tend to lie side by side to form fibres. Hair, hoofs, skin, nails, fibroin, muscle protein and wood are the examples of fibrous proteins.

The molecules of globular proteins are folded into compact units that often approach spheroidal shapes. These proteins are of great importance to living organisms since they act as catalysts for chemical reactions occurring in body cells. These catalytic agents are known as *enzymes* and their catalytic action is very specific. The enzymes bring about reactions in aqueous solution at room temperature and atmospheric pressure and under neutral conditions. They have complex protein structure.

SOME CHEMICAL CHARACTERISTICS OF PROTEINS

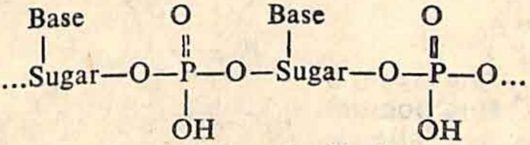
Most of the proteins in solution, when heated, undergo coagulation. This, phenomenon is known as *denaturation*, for as a result of this, the chemical nature of the protein is altered and they cannot be converted back to proteins. Coagulation of egg albumin (white of an egg) by heat is a familiar example of denaturation.

Concentrated acids bases, strong electrolytes and heavy metal ions (Hg^{2+}, Ag^{+}, etc.) also cause coagulation and denaturing.

Denatured proteins become useless for biological activity. Thus enzymes become ineffective when heated.

19.6. NUCLEIC ACIDS

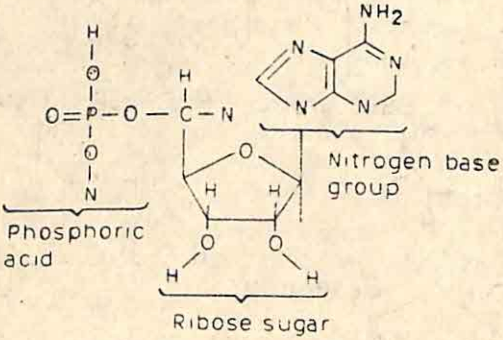
Nucleic acids are water-soluble high polymers formed in high concentration in the nucleic of living cells and are the substances which control heredity. They have also a long chain like proteins. In proteins, the long chains consist of polypeptides whereas in nucleic acids, the chain is polyester chain called *polynucleotide* chain. The polyester chain is derived from phosphoric acid (the acid portion) and sugar (the alcohol portion). The heterocyclic bases are also attached to the chain.



$$\ldots\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{O}-\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{OH}}{|}}{\text{P}}}-\text{O}-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{O}-\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{OH}}{|}}{\text{P}}}-\text{O}\ldots$$

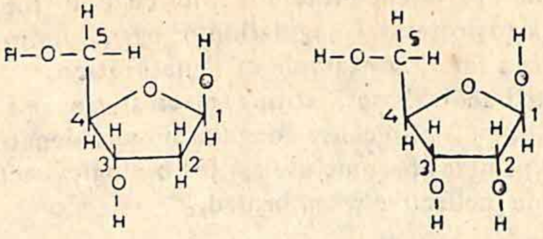
Polynucleotide chain

The structure of a common nucleotide, adenosine monophosphate, is shown:



Adenosine monophosphate

Nucleic acids are of two types depending upon the nature of the sugar. The sugar is either D-ribose in the group of nucleic acids known as RNA (*r*ibo*n*ucleic *a*cids) or D-2-deoxyribose (containing one less oxygen at the number 2 carbon than ribose) in the group known as DNA (*d*eoxyribo*n*ucleic *a*cids). These sugars are in the furanose form.



Deoxyribose Ribose

The RNA and DNA differ in nature of heterocyclic base, molecular weight, shape and in biological functions. The sugar units are joined to phosphate through the C – 3 and C—5 hydroxyl groups (Fig. 19.4). Some heterocyclic bases are joined to C—1 of

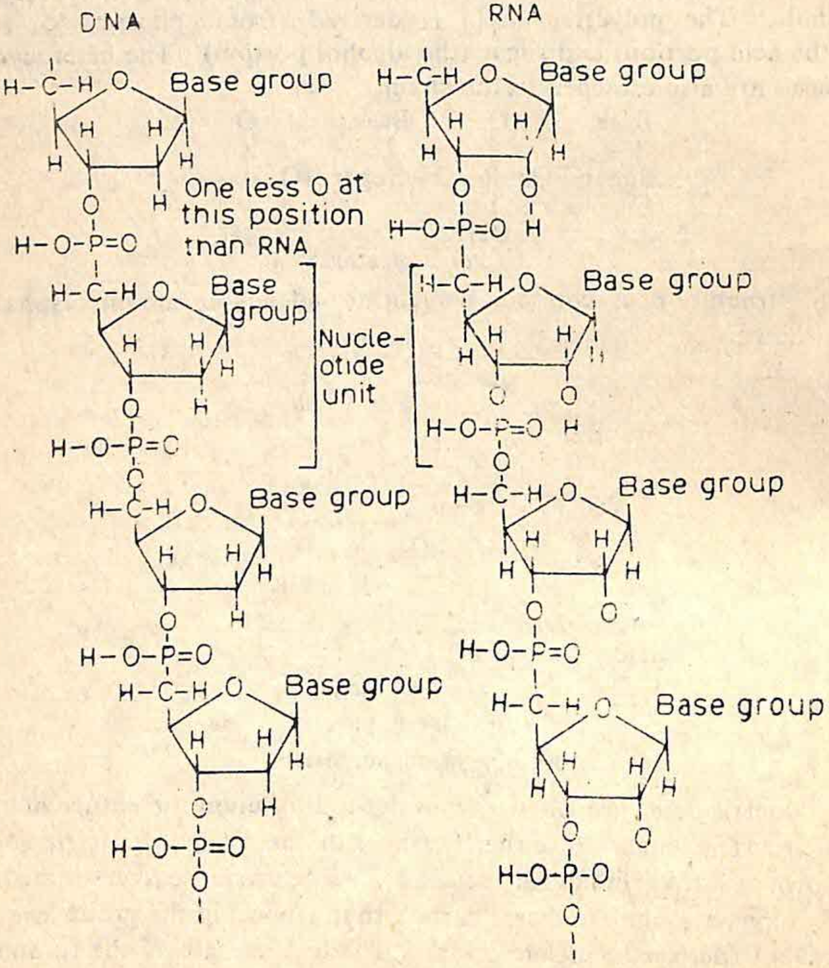
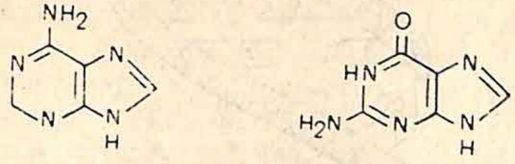


Fig. 19.4. The polynucletide structures of DNA and RNA.

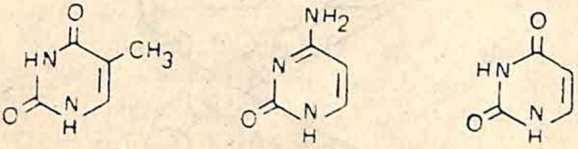
each sugar through a β-linkage. The most common bases found in nucleic acids are those belonging to purines (adenine and guanine) and pyrimidines (thymine, cytosine.and uracil).



Adenine

Guanine

(Purine bases)



Thymine

Cytosine

Uracil

(Pyrimidine bases)

The proportions of these heterocyclic bases and the sequence in which they follow each other along the polynucleotide chain differ from one kind of nucleic acid to another.

The secondary structure of DNA was given by Watson and Crick (1953) from chemical and X-ray data. Two polynucleotide chains, identical but heading in opposite directions, are wound or coiled about each other on a common axis to form a double helix, 18-20 Å in diameter (Fig. 19.5). The two strands are right-handed and have ten nucleotide residues per turn. They are held together at intervals by extensive hydrogen bonding between bases which occupy positions at right angles to the axis of the strands. The hydrogen bonds are formed between adenine and thymine and between guanine and cytosine. When such a pairing of bases between two coils or strands of DNA takes place, the two strands are said to be complementary to each other.

Functions of DNA

The macromolecule DNA is called the *master molecule* since it plays the key role in life processes. It supplies the cell with information and instructions as to how to prepare certain proteins and thus control the manufacture of proteins.

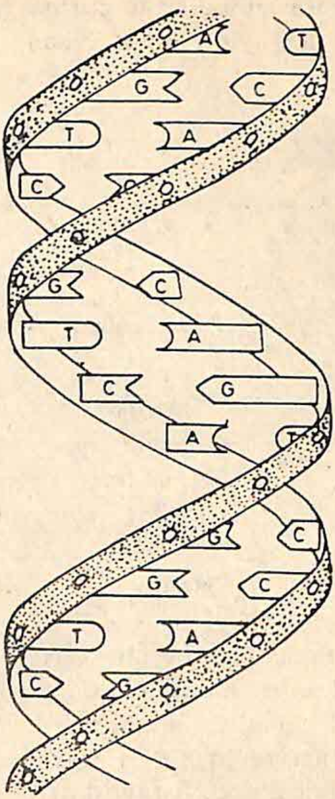


Fig. 19.5. The DNA double helix.

Cellular DNA has the property of precise self-replication. DNA is a reproducing molecule. Thus self-replication property of DNA is at the root of reproduction processes and forms the basis for the reproduction of a complete plant and animal.

DNA undergoes mutations, *i.e.*, becomes slightly or permanently altered in its nitrogenous base arrangement. This is carried out by the action of X-rays, γ-rays, ultraviolet light and certain chemicals. As a result of these changes, the structural and functional traits can change and these changes are shown in all cells of the plant or animal and its progeny.

The content of a cell in respect of some other chemicals may change under different environment, its DNA content remains constant.

Structure of RNA

As it has been said earlier, RNA differs from DNA in that the former contains the sugar ribose and the latter contains dexyribose. The bases adenine, guanine, cytosine and uracil are present in RNA while DNA has thymine and 2-methyl cytosine in place of uracil. The molecular masses of the two and their biological functioning are also different. RNA is a single strand molecule.

There are three types of RNA molecules in a cell which are used in protein synthesis. These are:

(i) Messenger RNA (m-RNA),
(ii) Ribosomal RNA (r-RNA) and
(iii) Transfer RNA (t-RNA).

The m-RNA is a complemementary copy of a segment of one strand of DNA. It carries the message of DNA for specific protein synthesis when required.

The r-RNA provides the necessary site for protein synthesis in the cytoplasm but does not carry any message of DNA.

The t-RNA transfers amino acids to the site of the protein synthesis. There are at least twenty different t-RNA molecules known to occur in the cell. Each of these molecules is specific for one amino acid.

EXERCISES

19.1 What are carbohydrates? Classify them and give their important properties.
19.2 How is a disaccharide obtained? Give three examples of disaccharide formation.
19.3 What are polysaccharides? How are they obtained?
19.4 Explain the phenomenon of photosynthesis of carbohydrates.
19.5 Give examples of various types of carbohydrates. What role do they play in living systems?
19.6 What are lipids? What role do they play in body functioning?
19.7 'Vitamins are vital for life', justify the statement.
19.8 Name important vitamins and give their dietary sources.
19.9 What are the diseases caused by the deficiency of vitamins A, B_1, B_2, B_6, B_{12}, C, D E and K?
19.10 What are hormones? Give the sources of secretion and principal functions of important hormones.
19.11 What are proteins? How are they classified?
19.12 Explain the primary and secondary structures of proteins.
19.13 What is the effect of heat and chemicals on proteins?
19.14 What are nucleic acids? How do they differ from proteins in their chain structure?
19.15 What are RNA and DNA? Point out the differences of the two.
19.16 Describe briefly the structure of DNA.
19.17 What are the functions of DNA?
19.18 What are the different types of RNA molecules in a cell? Give the utility of each.

Unit 20

Chemistry in the Service of Man

Some agricultural compounds. Polymers: Only important polymers like polythene, PVC, teflon, nylon, orlon, synthetic rubber, urea-formaldehyde resin, phenol-formaldehyde resin and bakelite (exculding their structures). Soaps and detergents. Medicinal compounds (structural aspects excluded).

The world population, especially in developing countries, is increasing at such a rapid rate that it has already reached an explosive stage. The problems already faced with the teeming millions of the world are too stupendous to be enumerated. The main problems are: (i) Food, (ii) Clothing, (iii) Housing and (iv) Disease. Chemistry is being used to overcome these vital problems of mankind. It has endeavoured to make life more comfortable and worth living. In this Unit, we shall deal with some important chemical products which are of immense use in the service of man.

20.1. AGRICULTURAL COMPOUNDS

Production of food can be increased by the application of two types of compounds in agriculture. These are: (i) Chemical fertilizers and (ii) Pesticides.

Chemical Fertilizers

It was found that the plants treated with bird droppings gave unprecedented yields. The analysis of the droppings showed that these contained nitrogen, phosphorus and potassium as the main constituents. Thus, it was concluded that these three elements are essential for the rich growth of the plants. Later on it was found that small amounts of other elements like calcium, magnesium, iron, sulphur, zinc, cobalt, molybdenum, etc., are also needed for plant nutrition. To provide the three most vital elements to the soil, there are three main types of chemical fertilizers: (1) Nitrogenous fertilizers, (2) Phosphate fertilizes and (3) Potash fertilizers.

(1) NITROGENOUS FERTILIZERS

Nitrogen produces rapid growth, increases yield, increases protein content, imparts dark green colour to leaves and improves quality of plants. Examples of nitrogenous fertilizers are ammonium sulphate, ammonium nitrate, calcium cyanamide, calcium ammonium nitrate (CAN) and urea. Of these CAN and urea are very safe and popular fertilizers. CAN is a stable, safe and non-hygroscopic fertilizer (nitrogen content: about 22%) and urea besides has also a higher percentage of nitrogen (nitrogen content: about 46%). These fertilizers provide nitrogen in the form of ammonia to the soil.

(2) PHOSPHATE FERTILIZERS

Phosphorus gives quick and vigorous start to plants, stimulates early root formation and growth, hastens maturity, helps formation of seed and increases resistance to frost.

Phosphorus is available in the form of mineral phosphates such as phosphorite and bone ash which chemically consist of $Ca_3(PO_4)_2$. But these are not suitable as fertilizers, being insoluble in water.

SUPERPHOSPHATE OF LIME

A mixture of calcium dihydrogen phosphate and calcium sulphate, it is a popular fertilizer as it is water-soluble. It is obtained by the action of calculated quantity of sulphuric acid on calcium phosphate.

$$Ca_3(PO_4)_2+2H_2SO_4+5H_2O \rightarrow \underbrace{Ca(H_2PO_4)_2.H_2O+2CaSO_4.2H_2O}_{\text{(Superphosphate of lime)}}$$

Another form of superphosphate known as *triple superphosphate* is manufactured these days. It enjoys the benefit of being free from calcium sulphate (inert material). It is obtained by the action of phosphoric acid on calcium phosphate (Fig. 20.1).

$$Ca_3(PO_4)_2+4H_3PO_4 \longrightarrow \underset{\text{Triple superphosphate}}{3Ca(H_2PO_4)_2}$$

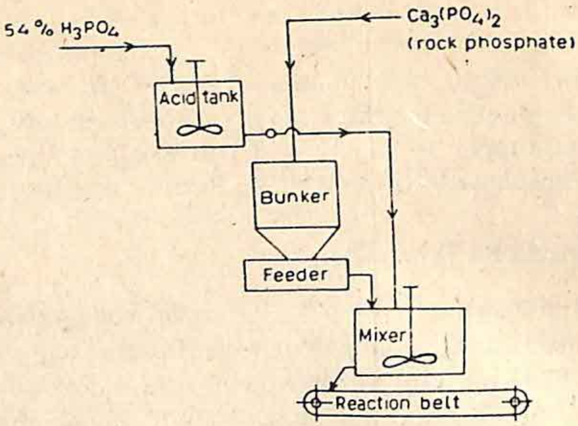


Fig. 20.1. Manufacture of triple superphosphate.

Besides these, phosphatic slags (from steel furnaces) and nitrophosphate are also used as phosphatic fertilizers.

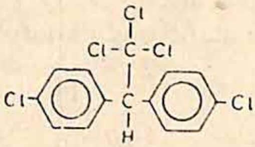
The strength of a phosphate fertilizer is measured on the basis of percentage of P_2O_5 available from it. Superphosphate of lime and triple superphosphate contain about 20 and 65% P_2O_5, respectively.

POTASH FERTILIZERS

Potassium counteracts undesirable effect due to the excessive use of other nutrients, especially that of nitrogen. It is required for the production of albuminoids and helps in the formation of carbohydrates. It increases vigour and disease resistance, makes stronger stalks and helps in the development of healthy roots. The common potassium fertilizers are potassium chloride (muriate of potash), potassium sulphate and potassium nitrate. For tobacco plants, potassium sulphate has been found to be more useful. It is because the ash of tobacco grown by using potassium sulphate has a high melting point while that obtained by using potassium chloride is easily fusible. Tobacco needed for making cigarettes should be high melting.

Pesticides

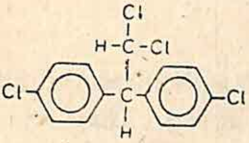
Pests are both plants and animals which are harmful to crops. Several types of undesirable weeds (herbs) and insects can ruin the desired crops. The chemical compounds which are used to destroy these undesirable herbs and insects are collectively called *pesticides* (*cide* from Latin *cido* which means *to kill*). The pesticides especially used to destroy herbs and insects are also called *herbicides* and *insecticides*, respectively. Similarly, we have *rodenticides*, *miticides*, *nematocides* and *fungicides* which are of particular use to destroy rodents, mites, nematodes and fungi, respectively. Some common pesticides are:



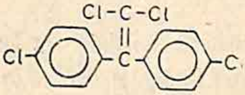
DDT

(*d*ichloro*d*iphenyl*t*richloroethane)

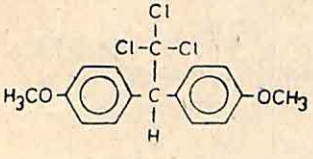
DDT is one of the most commonly used insecticides in spite of its harmful effects. It is much cheaper compared to other insecticides. However, some countries have banned its application.



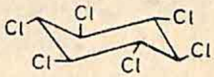
DDD



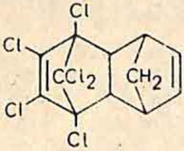
DDE



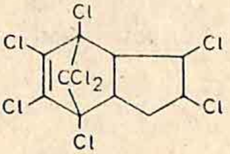
Methoxychlor



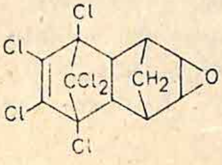
Gammexane; lindane or 666
(trade name: benzene hexachloride or BHC)



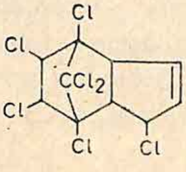
Aldrin



Chlordane



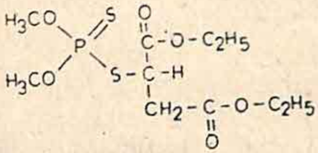
Dieldrin



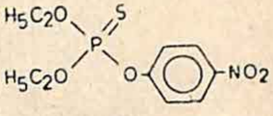
Heptachlor

The continuous use of insecticides has given rise to some problems, as well. The insects develop resistance and the insecticides get accumulated in animal bodies.

Organo-phosphatic pesticides form another class of pesticides. These are less stable and undergo degradation and thus require frequent application. However, they are more toxic and poisonous to insects. Common pesticides of this type include *malathion* and *parathion*. These pesticides are of fairly general action and are capable of killing both the useful and harmful insects.



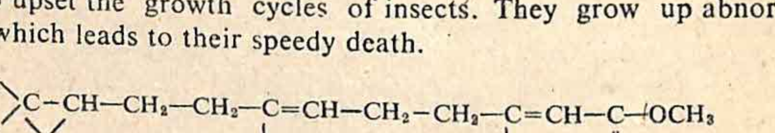
Malathion
(low toxicity)



Parathion
(toxic, half-life: 1-10 weeks)

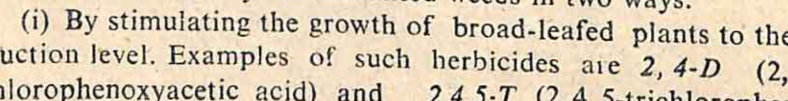
PHERMONES

These are chemicals exuded by some female insects to attract their males have also been used to control insects. These chemicals are effective in very small concentrations and specific in their action. An example of phermones is that of ***disparlure*** which has been used against gypsy moth.



Disparlure

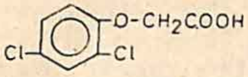
More recently, hormones like ***cecropia moth juvenile hormone*** are used to upset the growth cycles of insects. They grow up abnormally which leads to their speedy death.



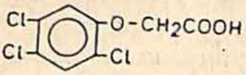
Cecropia moth juvenile hormone

Herbicides destroy the unwanted weeds in two ways:

(i) By stimulating the growth of broad-leafed plants to the destruction level. Examples of such herbicides are *2, 4-D* (2, 4-dichlorophenoxyacetic acid) and *2,4,5-T* (2, 4, 5-trichlorophenoxyacetic acid).

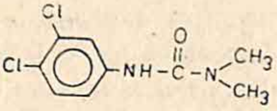


2,4-D



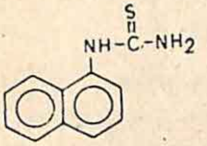
2,4,5-T

(ii) By stopping the photosynthesis of glucose in weeds. For example, *diuron* belongs to this class.

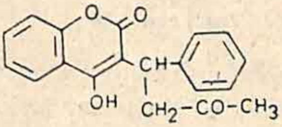


Diuron

Some rodenticides to kill rats (rodents) are zinc sulphide, barium carbonate, sodium fluoroacetate and sodium monochloroacetate. Examples of organic chemicals used for the purpose are *ANTU* (*a*lpha *n*aphthyl*t*hio*u*rea) and *warfarin* [3-α-acetonylbenzyl)-4-hydroxycoumarin].



ANTU



Warfarin

Some important fungicides are copper sulphate, copper naphthenate, Bordeaux mixture (copper sulphate+lime+water), 2, 4, 5-trichlorophenol and some mercury compounds.

20.2. POLYMERS

A *polymer* is an extremely large molecule (molecular weight ranging from say 5000 to one million or so) that is formed by linking a large number of small molecules together. The starting material of which a polymer is made is called a *monomer*. The process by which the polymers are formed is called *polymerization*.

Polymers are of two types :

(i) *Natural polymers*, such as proteins, polysaccharides (starch and cellulose), silk, wool, skin, rubber, gums, resins, etc.

(ii) *Synthetic polymers*, such as synthetic fibres (terylene, nylon) synthetic rubber, polyethylene, plastics, etc.

Now, we shall discuss some common synthetic polymers.

Manufacture of Synthetic Polymers

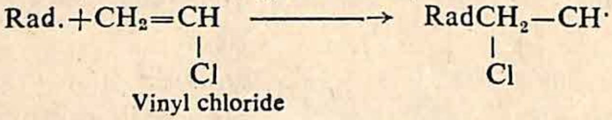
Synthetic polymers are manufactured by two types of processes:

ADDITION POLYMERIZATION

Here, the monomers are simply added together to form linear chains of the polymer. Addition polymerization continues by chain reactions that involve free radicals or ionic intermediates. Thus each step consumes a reactive particle (free radical or anion) and produces another similar particle to continue the chain. This type of polymerization is shown by ethylene and substituted ethylene. Thus vinyl chloride ($CH_2{=}CHCl$) polymerizes in the presence of a peroxide which provides a free radical to start the reaction:

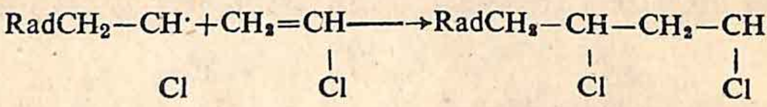
Chain initiating steps

(i) $\text{Peroxide} \longrightarrow \underset{\text{(Free radical)}}{\text{Rad.}}$

(ii) 

$$\text{Rad.} + \underset{\text{Vinyl chloride}}{CH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}}} \longrightarrow \text{Rad}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH^{\cdot}}}$$

Chain propagating steps

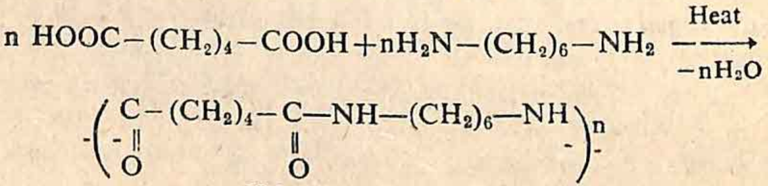
(iii) 

$$\text{Rad}CH_2{-}\underset{Cl}{CH^{\cdot}} + CH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow \text{Rad}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH^{\cdot}}}$$

Steps like (iii) are repeated to give $\text{Rad}(CH_2{-}CHCl)_n$ polyvinyl chloride (PVC). The polymers obtained by this mechanism are known as *addition polymers*.

CONDENSATION POLYMERIZATION

Here, the monomers are usually bifunctional (having two reaction sites) and the polymers are formed with the elimination of smaller molecules such as H_2O, NH_3, HCl or CH_3OH. Nylon is an example of condensation polymerization. Being a polymer of hexamethylene diamine and adipic acid, it is a *polyamide*.



$$n\,HOOC{-}(CH_2)_4{-}COOH + nH_2N{-}(CH_2)_6{-}NH_2 \xrightarrow[-nH_2O]{\text{Heat}} \left(\underset{\displaystyle O}{\underset{\|}{C}}{-}(CH_2)_4{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH{-}(CH_2)_6{-}NH\right)_n$$

Nylon 66

The numeral 66 indicates that each monomer molecule has six carbon atoms. The polymers obtained by this mechanism are known as *condensation polymers.*

Addition Polymers

POLYETHYLENE OF POLYTHENE

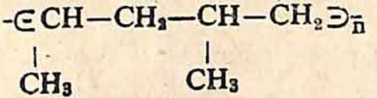
It is obtained from the monomer ethylene by subjecting it to a high pressure and high temperature. The reaction is initiated by oxygen or peroxides.

$$nCH_2{=}CH_2 \longrightarrow -\!\left(CH_2{-}CH_2{-}CH{-}CH_2\right)_{\overline{n}}$$

Polythene finds use in making pipes, laboratory apparatus, buckets, toys, films, etc. It is also used for insulation of electric wires.

POLYPROPYLENE

It is obtained from propylene, $H_2C{=}CHCH_3$.



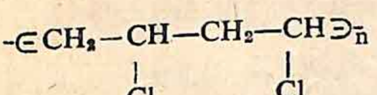
$$-\!\left(\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2\right)_{\overline{n}}$$

Polypropylene

This addition polymer is more tenacious and hard than polythene. it is used in the manufacture of milk cartons, ropes, fibres, pipes, etc.

POLYVINYL CHLORIDE (PVC)

It is obtained from the monomer vinyl chloride, $CH_2{=}CHCl$. It is used in the manufacture of pipes, raincoats, Shoes curtains, phonograph records, luggage, hand bags, floor tiles, etc. Because of the presence of chlorine atoms, PVC has lower flammability than polythene. It has good chemical and electrical resistance and is used in the manufacture of hose pipes and insulators for wires, cables, etc.



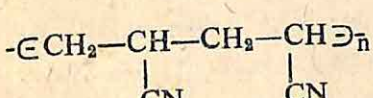
$$-\!\left(CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}\right)_{\overline{n}}$$

PVC

POLYACRYLONITRILE (ORION)

It is obtained from acrylonitrile, $CH_2{=}CHCN$.

The polymer is used in the manufacture of textiles, rugs and orlon and acrilan fibres.

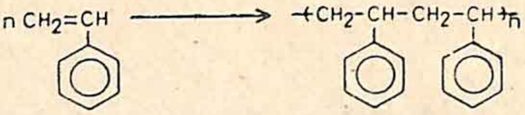


$$-\!\left(CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}{-}CH_2{-}\underset{\displaystyle CN}{\underset{|}{CH}}\right)_{\overline{n}}$$

Polyacrylonitrile

POLYSTYRENE

It is obtained from the monomer styrene.

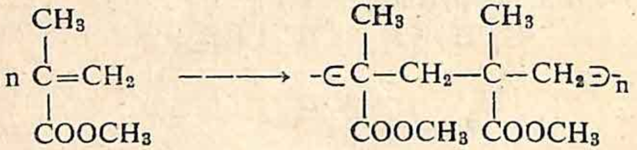


Styrene Polystyrene

Polystyrene is a transparent polymer and is used in the manufacture of containers, toys, household wares, refrigerators and television bodies, styrofoam, etc.

POLYMETHYLMETHYLACRYLATE (PMMA)

It is an addition polymer of methylmethylacrylate. It is an extremely clear polymer and possesses excellent light transmission. It is sold under various commercial names like *plexiglass*, *arylite*, *perspex* and *lucite*.



$$n\ \overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}=CH_2 \longrightarrow -\in \overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}-CH_2\ni_n$$

Methylmethylacrylate Polymethylmethylacrylate

PMMA is used in the manufacture of lenses, plastic jewellery, lamp shades, etc. As it can be easily coloured and tinted, it finds wide application in moulded novelties, signboards and for decoration.

POLYTETRAFLUOROETHYLENE (TEFLON)

It is obtained from tetrafluoroethylene.

$$n\ CF_2=CF_2 \longrightarrow -\in CF_2-CF_2-CF_2-CF_2\ni_n$$

Tetrafluoroethylene Teflon

Teflon resists the action of acids, alkalies and oxidizing agents. It is an extremely inert polymer and stable towards high temperature. It is used in the manufacture of gaskets, seals, non-lubricated bearings, filter clothes, etc. It is also used in non-stick pan coatings.

SYNTHETIC RUBBERS

Rubber is an elastic polymer, *i.e.*, it stretches on application of force and comes back to original shape on removing the force.

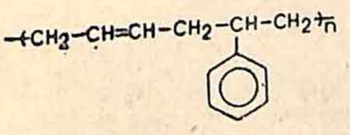
Natural rubber (obtained from the latex of the rubber trees) is a polymer of isoprene and may be represented as:

$$-\!\left(\mathrm{CH_2{-}C{=}CH{-}CH_2}\right)\!-_n$$

A large number of synthetic rubbers have been developed which are more useful than the natural rubber. Two common types of synthetic rubbers are buna-S and neoprene.

BUNA-S

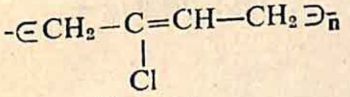
It is obtained by co-polymerization of butadiene and styrene in presence of polymerizing agent, Na, sodium. (Buna-S=*Bu*tadiene +*Na*+Styrene). It is used in automobile tyres, belts, hose pipes, flooring and rubber shoe soles.



Buna-S

NEOPRENE

It is the first American synthetic rubber (1932) obtained from chloroprene by free radical addition polymerization. It is used for making shoe heels, belts, stoppers, etc.



$$-\!\left(\mathrm{CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2}\right)\!-_n$$

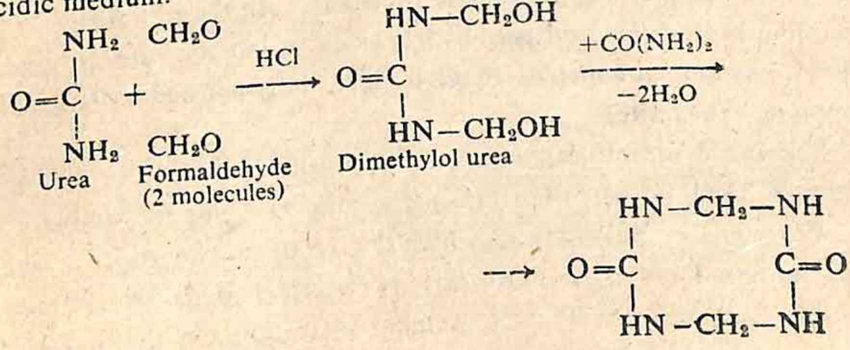
Neoprene

Other synthetic rubbers include buna-N (monomers: butadiene+acrylonitrile) and butyl rubber (monomers: isobutylene+isoprene).

Condensation polymers

UREA-FORMALDEHYDE RESINS

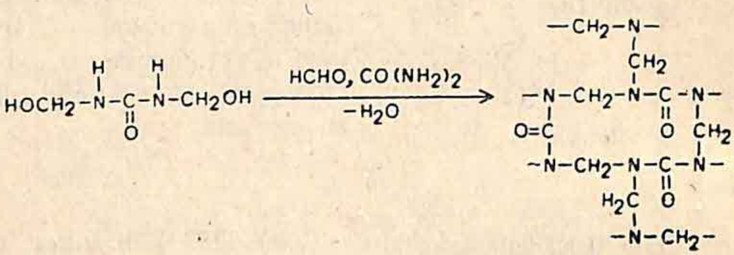
These are obtained by condensation of urea and formaldehyde in acidic medium.



$$\underset{\text{Urea}}{\mathrm{O{=}C(NH_2)_2}} + \underset{\substack{\text{Formaldehyde}\\ \text{(2 molecules)}}}{\mathrm{2\,CH_2O}} \xrightarrow{\mathrm{HCl}} \underset{\text{Dimethylol urea}}{\mathrm{O{=}C(HN{-}CH_2OH)_2}} \xrightarrow[-2\mathrm{H_2O}]{+\mathrm{CO(NH_2)_2}} \mathrm{O{=}C\begin{matrix}\mathrm{HN{-}CH_2{-}NH}\\ \mathrm{HN{-}CH_2{-}NH}\end{matrix}C{=}O}$$

Unpolymerized resins are colourless and soluble in water. These are extensively used as adhesives for paper, cloth and wood.

The polymerized resins are hard, chemically inhert and resist the attack of solvents. They are thermosetting and cannot be reshaped by heating.



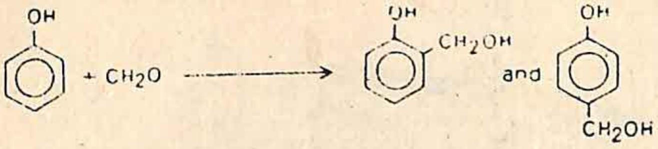
Polymerized resin

Polymerized resins are mostly used in moulded plastics.

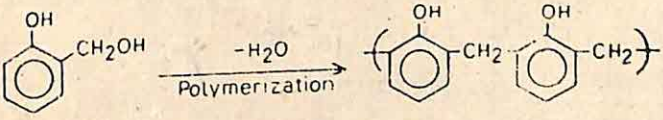
PHENOL-FORMALDEHYDE RESINS (BAKELITE)

These are formed by condensation polymerization of formaldehyde and phenol in presence of an acid or alkali. In the initial stage of reaction, both *ortho-* and *para*-hydroxymethyl phenols are formed. These phenols polymerize to give linear polymer and crosslinked copolymer (bakelite).

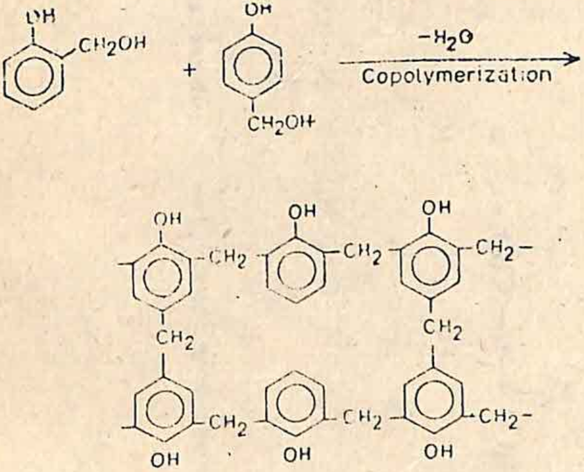
Bakelites with low degree of polymerization are soft in nature and are used in varnishes, lacquers and as a glue for laminated wooden planks. Bakelites with high degree of polymerization are hard in nature and are used for making electrical goods, phonograph records, fountain pen barrels, combs, etc. Sulphonated bakelite polymers are used as ion-exchange resins.



Phenol Formaldehyde *o*- and *p*-hydroxymethyl phenols.



Linear polymers



Crosslinked copolymer bakelite.

NYLON

The polyamide obtained by condensation of a dibasic acid and a diamine is called *nylon*. For example, *nylon 66* is made by condensation polymerization of adipic acid and hexamethylenediamine.

Nylon makes extremely strong threads and fibres because its long chain molecules have stronger intermolecular forces. Each N—H group in a nylon chain is hydrogen bonded to a C=O group in a neighbouring chain (Fig. 20.2).

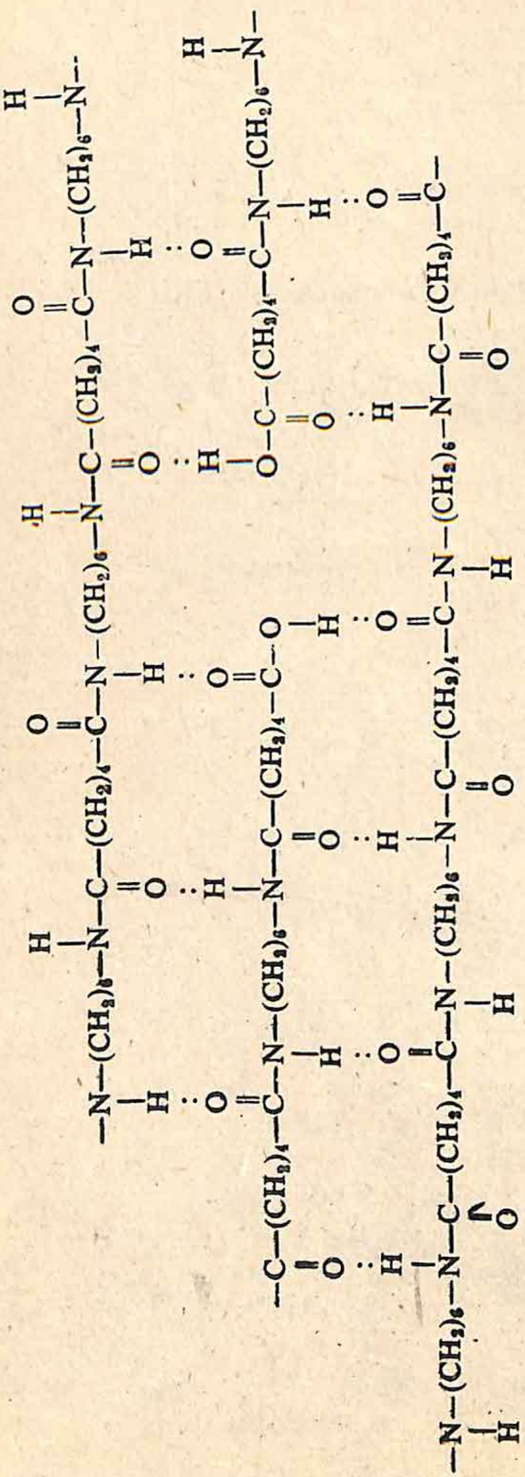
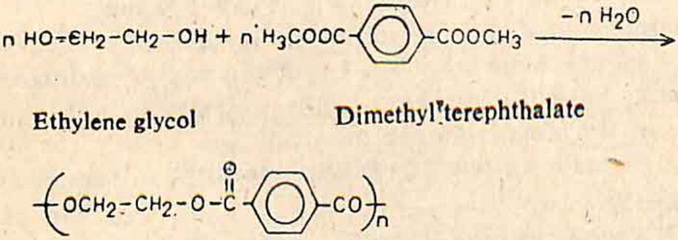


Fig. 20.2. Strong hydrogen bonding between polymer chains in nylon.

Nylon has a very high tensile strength and is tough, flexible, resistant to abrasion and somewhat elastic. It is used in carpets, fabrics and in machine parts. It is also used in elastic hosiery and for bristles of brushes.

TERYLENE OR DACRON

It is a *polyester* obtained by condensation polymerization of ethylene glycol and dimethyl terephthalate in the presence of a weak base such as calcium acetate.



Ethylene glycol

Dimethyl terephthalate

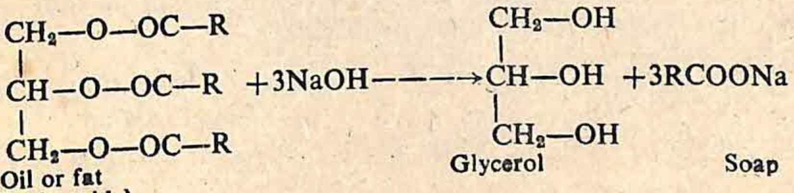
Terylene or dacron

Terylene is crease-resistant and has a low moisture content. It is used for wash and wear fabrics. Further, due to its high tensile strength and resistance to tearing, it is used for making magnetic recording tapes.

20.3. SOAPS AND DETERGENTS

Soaps

Soaps are usually the mixtures of sodium or potassium salts of long-chain fatty acids present in oils and fats. These are obtained by the alkaline hydrolysis of oils and fats (glycerides). The process of hydrolysis of oils and fats is known as *saponification.*



$$\begin{array}{l} CH_2-O-OC-R \\ | \\ CH-O-OC-R \\ | \\ CH_2-O-OC-R \end{array} + 3NaOH \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3RCOONa$$

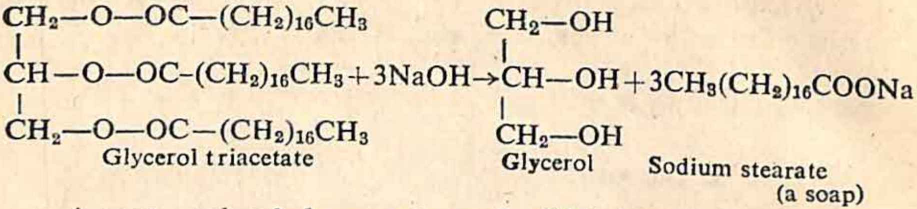
Oil or fat
(a glyceride)

Glycerol

Soap

(where $R = C_{17}H_{35}$, $C_{17}H_{33}$, $C_{17}H_{31}$, $C_{15}H_{31}$, $C_{13}H_{27}$, $C_{11}H_{23}$, etc.)

for example:



$$\begin{array}{l} CH_2-O-OC-(CH_2)_{16}CH_3 \\ | \\ CH-O-OC-(CH_2)_{16}CH_3 \\ | \\ CH_2-O-OC-(CH_2)_{16}CH_3 \end{array} + 3NaOH \rightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 3CH_3(CH_2)_{16}COONa$$

Glycerol triacetate   Glycerol   Sodium stearate (a soap)

A soap molecule has a polar end, $-COO^-Na^+$ and a non-polar end, the long chain of 11 to 17 carbon atoms. The polar end is water-soluble and is said to be *hydrophilic* (water-loving). The non-polar end is water-insoluble and is called *hydrophobic* (water-hating). It is, of course, soluble in non-polar solvents. The polar ends project outward into the polar solvent, water.

Soap is a good washing agent and possesses the advantage of being completely biodegradable, i.e., it can be fully oxidized by micro organisms present in sewage. It thus possesses no pollution problem. However, it suffers from two disadvantages:

(i) It forms a white curdy precipitate with hard water and is thus wasted.

(ii) It cannot be used in acidic medium as the acids precipitate the insoluble free fatty acids which stick to the fabric and check their dyeing.

Detergents

Since 1940's *synthetic detergents* have replaced soaps in many applications. Unlike soaps, the detergents maintain their efficiency even in hard water as their calcium or magnesium salts are soluble. Also, being salts of strong acids, they yield neutral solutions whereas soaps, being salts of weak acids, yield slightly alkaline solutions. However, many detergents are not completely bio-degradable and cause water pollution. Like soaps, detergents also have a large non-polar hydrocarbon end that is oil-soluble and a polar end that is water-soluble.

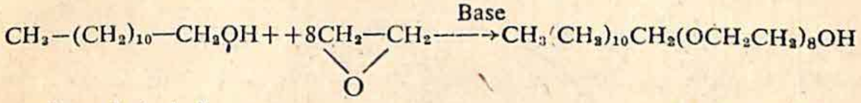
Sodium alkyl suphates form an important class of *ionic detergents* which are made by reacting a long chain alcohol such as lauryl alcohol with sulphuric acid and then neutralizing the resulting alkyl sulphate with sodium hydroxide.

$$\underset{\text{n-Lauryl alcohol}}{CH_3(CH_2)_{10}CH_2-OH} + H_2SO_4 \longrightarrow \underset{\text{Lauryl sulphate}}{CH_3(CH_2)_{10}CH_2-OSO_3H}$$

$$CH_3(CH_2)_{10}CH_2-OSO_3H + NaOH \dashrightarrow \underset{\text{Sodium lauryl sulphate}}{CH_3(CH_2)_{10}CH_2-OSO_3^-Na^+} + H_2O$$

NONIONIC DETERGENTS

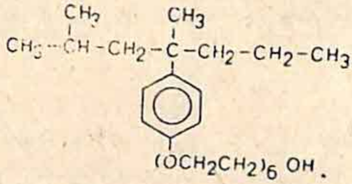
Non-ionic detergents like ethoxylates these can be prepared by treating aliphatic alcohols with ethylene oxide in the presence of a base. For example:



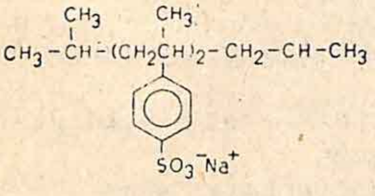
$$CH_3-(CH_2)_{10}-CH_2OH++8\underset{O}{CH_2-CH_2}\xrightarrow{\text{Base}}CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_8OH$$

n-Lauryl alcohol An ethoxylate

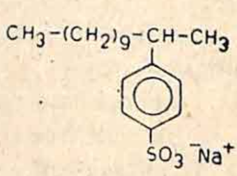
Another non-ionic ethoxylated detergent obtained from nonylpheol and ethylene oxide can be formulated as:



Alkyl benzene sulphonates are toxic detergents and are not completely biodegradable. These are obtained by conversion of benzene into corresponding alkyl benzene followed by sulphonation with sulphuric acid and neutralization with sodium hydroxide. Two examples are given below:



Alkyl benzene sulphonate (ABS)



Linear alkyl benzene sulphonate (LAS)

Cleaning Action of Soaps and Detergents

The problem in cleaning is the oil and grease that make up and contain the dirt. Water alone cannot dissolve these hydrophobic or non-polar substances. Soap or detergent has a polar part $-COO^-Na^+$ or $-SO_3^-Na^+$ and a non-polar part of long hydrocarbon chain. When the object is rubbed with soap or agitated with soap or detergent solution, the non-polar ends dissolve in the oily droplets on the dirt while the polar ends remain in the water layer. Each oily droplet is now surrounded by negative $-COO^-$ or $-SO_3^-$ ions. The oil droplets remain dispersed and a stable emulsion is formed. Thus the oil or grease containing dirt is emulsified and is washed away with water (Fig. 20.3). Soaps and detergents are, therefore, typical surface-active agents and lower the surface tension of a liquid or the interfacial tension between liquids.

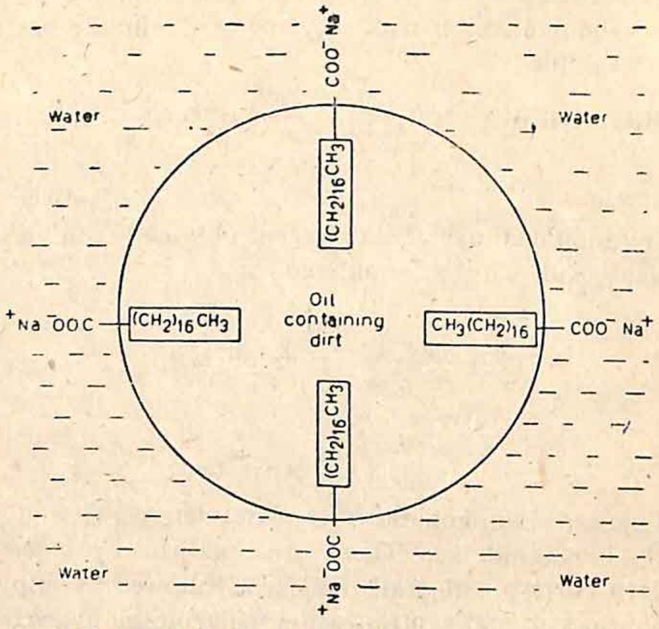


Fig. 20.3 Cleaning action of soap or detergent.

20.4. MEDICINAL COMPOUNDS

Medicines or drugs are the chemical compounds that help humanity in a number of ways:

- (i) To check and prevent disease and thus make life comfortable and free from pain.
- (ii) To increase the life span of human beings.
- (iii) To check the population explosion.

These compounds can be broadly classified as under:

Antiseptics

These are both bacteriostatic and bacteriocidal, i.e. , prevent the growth of micro-organisms and may also kill them. These are applied to wounds, ulcers and infected skin surface.

Disinfectants

These compounds can kill micro-organisms but they are harmful when brought in contact with human tissues. They are used to kill micro-organisms in floors, toilets, instruments, etc. It may be noted that the same substance can be used as an antiseptic as well as a disinfectant depending upon its concentration. Thus, phenol in lower concentration acts as an antiseptic while in higher concentration as a disinfectant.

Germicides

These are the chemicals which can kill or destroy various germs, fungi and viruses.

The chemicals used as antiseptics, disinfectants and germicides are usually metabolic poisons or oxidizing agents. Some of these are given below:

Poisons

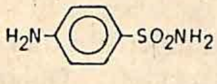
Mercuric chloride solution (0.1%), phenol, cresols, resorcinols, salicylic acid, picric acid, silver nitrate, boric acid, acriflavine, DDT, formaldehyde, etc.

Oxidizing Agents

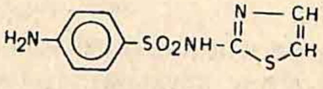
Potassium permanganate solution (1%), hydrogen peroxide solution (3%), bleaching powder, sodium hypochlorite solution, iodoform, tincture of iodine, etc.

20.5. CHEMOTHERAPY

The term *chemotherapy* is applied to the treatment of any disease by the use of chemical compounds. Ehrlich used the term for the first time when he was searching for some chemical that could cure syphilis. An ideal chemotherapeutic agent should be so selective as to kill the invading micro-organisms without producing any harmful side-effects on body issues or organs. Some well known chemotherapeutic drugs are:

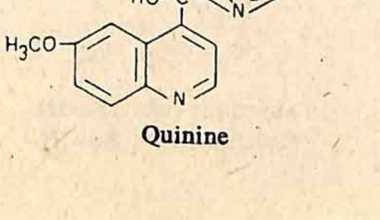


Sulphanilamide



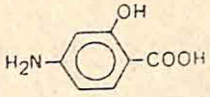
Sulphathiazole

(These and other sulpha drugs like sulphadiazine, sulphapyridine, etc., are effective in inhibiting the growth of bacteria within the body. They are used for sore throat infections, boils, bronchitis, etc.)

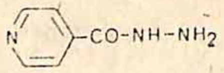


Quinine

(Quinine and other compound like pamaquine and chloroquine are used to control malarial fever.)



PAS (*p*-amino salicylic acid)



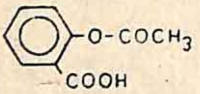
INH (*iso*-nicotin hydrazine)

(These are used for the treatment of tuberculosis.)

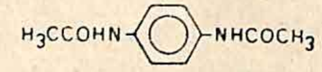
Let us study more of chemotherapeutic drugs under different heads:

Antipyretics

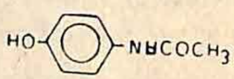
These are the drugs which lower body temperature in case of high fever. Some common examples are aspirin (acetyl salicylic acid), phenacetin, novalgin (analgin), *para*-acetamol (4-acetamidophenol) etc.



Aspirin
(acetyl salicylic acid)



Phenacetin

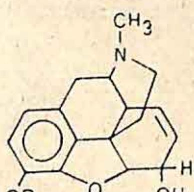


para-Acetamol
(4-acetamidophenol)

The indiscriminate use of these drugs should be avoided. They should not be taken on an empty stomach as they may ulcerate the stomach.

Analgesics

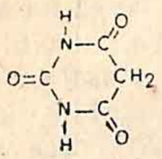
These are pain relieving drugs sold under different trade names such as aspro (aspirin), novalgin, saridon, anacin, etc. Opium alkaloids which include morphine, codeine and heroin are also used as analgesics. But these are habit-forming and are sold only under medical advice.



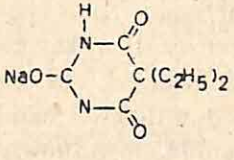
Morphine (when R=H)
Codeine (when R=CH_3)

Tranquilizers and Hypnotics

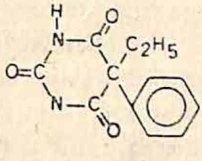
These drugs help to reduce anxiety in patients by acting on the central nervous system. They are sleep-inducing and may become habit-forming. Barbituric acid derivatives are among the best known and most widely used hyponotics.



Barbituric acid

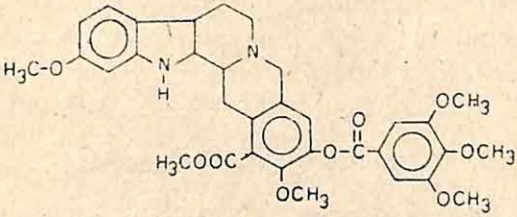


Veronal
(sodium barbital)



Luminal
(phenobabital)

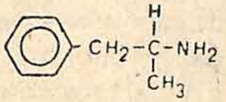
Serpasil (reserpine), a drug obtained from an Indian plant *Raowolfia Serpentina*, is a powerful tranquilizer.



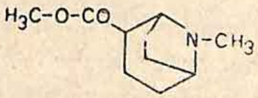
Serpasil (reserpine)

Antidepressants

These drugs, when taken, give a feeling of well-being and enhance self confidence by acting on the nervous system. They are known as 'mood boosters'. It is better to use them under medical advice. Tofranil and benzedrine are typical examples of antidepressants. The alkaloid cocaine can also act as mood elevator.



Benzedrine

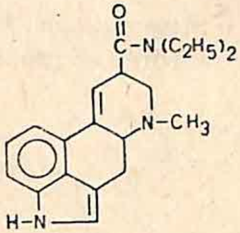


Cocaine

Psychedelic Drugs

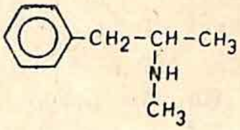
These drugs cause hallucinations, disturb vision and hearing. One loses a sense of time and space and the individual feels a false sense of happiness. One observes colours which are actually not there. Such drugs leave a very adverse effects on both mind and body. An important drug of this type is LSD (lysergic acid diethylamide).

It was the year 1943. A Swiss chemist while working in the laboratory, consumed his lunch there. As soon as he finished his lunch, he felt very strange. He went to the doctor who was equally puzzled by his symptoms which were a mixture of hallucinations and unnatural sensory distortions. The symptoms lasted for several hours. The chemist later on recalled that he had momentarily kept his sandwich on the laboratory bench top where it had picked up micro amounts of a compound that he had been working with. It was *d*-lysergic acid diethylamide, now known as LSD. The chemist had accidently taken the first 'trip' himself with the compound.



LSD (lysergic acid diethylamide)

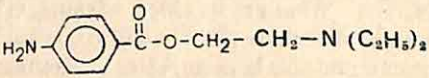
Methamphetamine (known as 'speed') and marijuana (known as 'pot', 'grass' or 'maryjane') are also similar drugs and their sales are restricted or prohibited.



Methamphetamine

General Anaesthetics

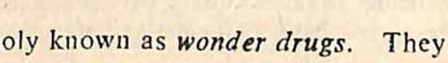
These drugs cause a loss of sensation and consciousness and the patient does not have the feeling of pain. They are used for major surgical operations. Some of them act after absorption of vapours or gas through lungs. These are diethyl and divinyl ethers, nitrous oxide (laughing gas), cyclopropane and ethylene. Some drugs are also injected into the body. These are morphine, pathedine, etc. There are drugs that are injected or applied locally to produce insensibility to pain in a limited area or portion of the body. These are called *local anaesthetics* and are used for minor surgical operations like tooth extraction or stitching of a small wound. Common examples are of cocaine, procaine and xylocaine. Ethyl chloride is sprayed locally. It evaporates and causes intense cooling of the part to be operated upon.



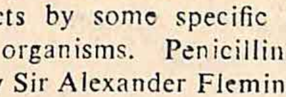
Procaine

Antibiotics

These are commoly known as *wonder drugs*. They are produced as metabolic products by some specific living organisms and can be used to kill other organisms. Penicillin is the first antibiotic which was discovered by Sir Alexander Fleming in 1929. This is an effective drug against pneumonia, bronchitis, abcesses, sore throat, etc. Chloromycetin is used for the treatment of typhoid. Streptomycin is used for the treatment of tuberculosis. These days many new broad-spectrum antibiotics are in use which are effective against different types of micro-organisms. Such antibiotics are tetracyclin, tetramycin, ampicillin, etc.



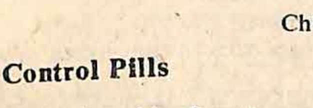
Penicillin



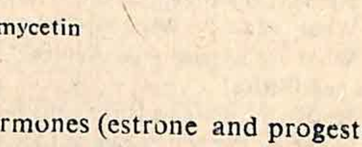
Chloromycetin

Birth Control Pills

These are related to female sex hormones (estrone and progestrone). The commoly used pills contain norethindrone and mestranol. These drugs are found to have side effects and should be taken under medical observation.



Norethindrone



Mestranol

EXERCISES

20.1 What are agricultural compounds?
20.2 Name a few chemical fertilizers containing nitrogen, phosphorus and potassium and give their chemical formulae.
20.3 What is CAN? What are its chief advantages?
20.4 How are superphosphate of lime and triple superphosphate prepared?
20.5 Why is potassium sulphate superior to potassium chloride for tobacco plant?
20.6 Discuss the importance of nitrogen, phosphorus and potassium for the better growth of crops.
20.7 What are insecticides and herbicides? Give two examples of each.
20.8 What are organo-phosphatic pesticides and phermones? Give one example of each.
20.9 What are polymers? How are they classified?
20.10 How are the polymers manufactured?
20.11 Write notes on:
(i) Polythene (ii) PVC (iii) Teflon
(iv) Nylon (v) Orlon (vi) Plexiglass
20.12 Name two synthetic rubbers and write their formulae.
20.13 What are condensation polymers? How are urea-formaldehyde resins and phenol-formaldehyde resins obtained?
20.14 How is bakelite obtained? What are its uses?
20.15 What are soaps? Give their uses and drawbacks.
20.16 What are detergents? What similarity have they got with soaps?
20.17 How are soaps and detergents manufactured?
20.18 Explain the cleaning action of soaps and detergents.
20.19 How do the medicinal compounds help the mankind?
20.20 What are antiseptics, disinfectants and germicides? Give examples of each.
20.21 What is chemotherapy? Give some examples of chemotherapeutic drugs.
20.22 What are antipyretics and analgesics? Give two examples in each case.
20.23 What are the best known hypnotics used? How do they act in the body?
20.24 Name two antidepressants. What is their use?
20.25 What is LSD? What are its adverse effects?
20.26 What are general anaesthetics? How are they distinguished from local anaesthetics?
20.27 Justify the statement that antibiotics are the wonder drugs of today.
20.28 Name a drug which can be used against:
(i) Malaria (ii) Fever (iii) Flue
(ii) Depression (v) Typhoid (vi) Pneumonia
(vii) Bronchitis (viii) Tuberculosis (ix) Sore throat
20.29 Why should the birth control pills be taken under medical advice? What are the chemical compounds contained in the pills?

A PERIODIC CLASSIFICATION OF ELEMENTS

1	2											3	4	5	6	7	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 see below*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 see below†	104	105													

*LANTHANIDE SERIES	57 La		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
†ACTINIDE SERIES	89 Ac		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Atomic Numbers and Relative Atomic Masses*

Name	*Symbol*	*Atomic Number*	*Relative Atomic Mass*
Actinium	Ac	89	227.0278
Aluminium	Al	13	26.981 54
Americium	Am	95	—
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	—
Barium	Ba	56	137.33
Berkelium	Bk	97	—
Beryllium	Be	4	9.012 18
Bismuth	Bi	83	208.9804
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.41
Caesium	Cs	55	132.9054
Calcium	Ca	20	40.08
Californium	Cf	98	—
Carbon	C	6	12.011
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	—
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	—
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	—
Fluorine	F	9	18.998 403
Francium	Fr	87	—
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.9665
Hafnium	Hf	72	178.49
Helium	He	2	4.002 60
Holmium	Ho	67	164.9304
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.9045
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	—
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.967
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.9380

---

*Relative atomic masses are based on $^{12}C=12$

(Contd)

Name	*Symbol*	*Atomic Number*	*Relative Atomic Mass*
Mendelevium	Md	101	—
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.179
Neptunium	Np	93	237.0482
Nickel	Ni	28	58.70
Niobium	Nb	41	92.9064
Nitrogen	N	7	14.0067
Nobelium	No	102	—
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.973 76
Platinum	Pt	78	195.09
Plutonium	Pu	94	—
Polonium	Po	84	—
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.9077
Promethium	Pm	61	—
Protactinium	Pa	91	231.0359
Radium	Ra	88	226.0254
Radon	Rn	86	—
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.9055
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.4
Scandium	Sc	21	44.9559
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.868
Sodium	Na	11	22.989 77
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.9479
Technetium	Tc	43	—
Tellurium	Te	52	127.60
Terbium	Tb	65	158.9254
Thallium	Ti	81	204.37
Thorium	Th	90	232.0381
Thulium	Tm	69	168.9342
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.029
Vanadium	V	23	50.9415
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.9059
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences 1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1228	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	1	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

S.C.E.R.T, West Bengal
Library
Calcutta
25 B. Road

540

OUTLINES OF CHEMISTRY is a text recommended by the Central Board of Secondary Education vide its letter no. Acad II/Gr. II/P.F./86/9679

The book is geared to meet the requirements of Class XII students. It is divided into 20 units and covers the vast spectrum of the new syllabus. Each chapter contains worked out examples, problems to solve and a brief summary of the chapter. The book has a simple approach. It discusses the various topics precisely and gives the student only the relevant information. It is an ideal text for a one-year course.

Dr M Katyal is a lecturer at St Stephen's College, Delhi University and has been teaching undergraduate students for over 20 years. After receiving his PhD from Delhi University, he was a post-doctoral fellow at Dalhousie and Carleton and visiting scientist at Waterloo and Moncton Universities in Canada. He has over a dozen published books and research monographs to his credit.

R P Katyal is presently the Principal, Government College, Rohtak. He has teaching experience of over 30 years and has written a number of textbooks for undergraduate as well as intermediate levels.

OTHER BOOKS IN CHEMISTRY

EXPERIMENTS IN CHEMISTRY for Class XII
Chhatwal, Katyal and Dudeja

INVESTIGATORY PROJECTS IN CHEMISTRY
A K Chakravarty

CHEMISTRY for Class XI
Banerjee, Trikha and Nayar

EXPERIMENTS IN CHEMISTRY for Class XI
Chhatwal, Katyal and Munjal

Tata McGraw-Hill Publishing Company Limited
12/4 Asaf Ali Road, New Delhi 110 002

Rs. 20.00

25P00

0-07-096471-8